Change in local order of $TM_{80-x}RE_xMe_{20}$ amorphous alloys: a structural model

Change in local order of TM$_{80-x}$RE$_x$Me$_{20}$ amorphous alloys: a structural model

F Machizaud†, G Ravach‡, J Teillet‡§ and J M Le Breton‡

† LSG2M, UMR CNRS 7584, Ecole des Mines de Nancy, Parc de Saurupt,
F-54042 Nancy Cédex, France
‡ GPM, Magnétisme et Applications, UMR CNRS 6634, Université de Rouen,
F-76821 Mont-Saint-Aignan Cédex, France

E-mail: `jacques.teillet@univ-rouen.fr`

Abstract. The local order in TM$_{80-x}$RE$_x$Me$_{20}$ (TM = transition metal, RE = rare earth, Me = metalloid) amorphous alloys is investigated by considering two limit cases: either (TM$_{80-x}$Me$_{20}$)RE$_x$, where the alloy would be a dilute solution of RE atoms in a (TM$_{100-y}$Me$_y$) distorted prismatic network, or (TM$_{80-x}$RE$_x$)Me$_{20}$, where the alloy would be a dilute solution of RE atoms in a polytetrahedral compact network of TM atoms containing interstitial Me atoms. The comparison of the calculated atomic pairs with the experimental results provides evidence for a critical RE concentration range close to 8–9 at.%. This is in agreement with a previous Mössbauer study of Fe$_{80-x}$RE$_x$B$_{20}$ amorphous alloys, which pointed out a structural modification of the iron environments in this rare earth concentration range.

1. Introduction

Ternary amorphous systems containing transition metal (TM), rare earth (RE) and metalloid elements (Me), particularly with compositions such as TM$_{80-x}$RE$_x$Me$_{20}$, have been extensively studied [1]. Mössbauer studies of melt-spun Fe$_{80-x}$RE$_x$B$_{20}$ amorphous ribbons revealed that the values and the variations of the mean hyperfine field are insensitive to the nature of the rare earth when RE is Pr, Gd or is substituted by Y [2, 3]. Recently, we performed a Mössbauer investigation of melt-spun Fe$_{80-x}$RE$_x$B$_{20}$ amorphous ribbons with RE = Dy, Ho, Nd in the composition range $x \leqslant 16$ at.% [4–6]. Not only did we observe the same result, but we found evidence for a drastic discontinuity in the variation of the mean hyperfine parameters with the rare earth concentration, occurring around $x = 8$–9 at.% whatever the nature of the rare earth atom. We attributed this discontinuity to a strong modification of the local order around Fe atoms in this composition range. In order to identify this modification, we carefully investigated the crystallization process for two amorphous alloys, with rare earth concentration lying below (Fe$_{74}$Dy$_6$B$_{20}$) and above (Fe$_{70}$Dy$_{10}$B$_{20}$) the critical concentration x_c [7]. With the assumption of a correlation between the local order of the amorphous state and the nature of the first crystallization product, our results on Fe$_{74}$Dy$_6$B$_{20}$ alloy suggest the existence of local iron environments of t-Fe$_3$B type, as in amorphous Fe$_{80}$B$_{20}$. In Fe$_{70}$Dy$_{10}$B$_{20}$, local iron environments seem more complex, involving probably dysprosium atoms. Such a

§ Corresponding author: Professor J Teillet, GPM, Magnétisme et Applications, UMR CNRS 6634, Université de Rouen, F-76821 Mont-Saint-Aignan Cédex, France.
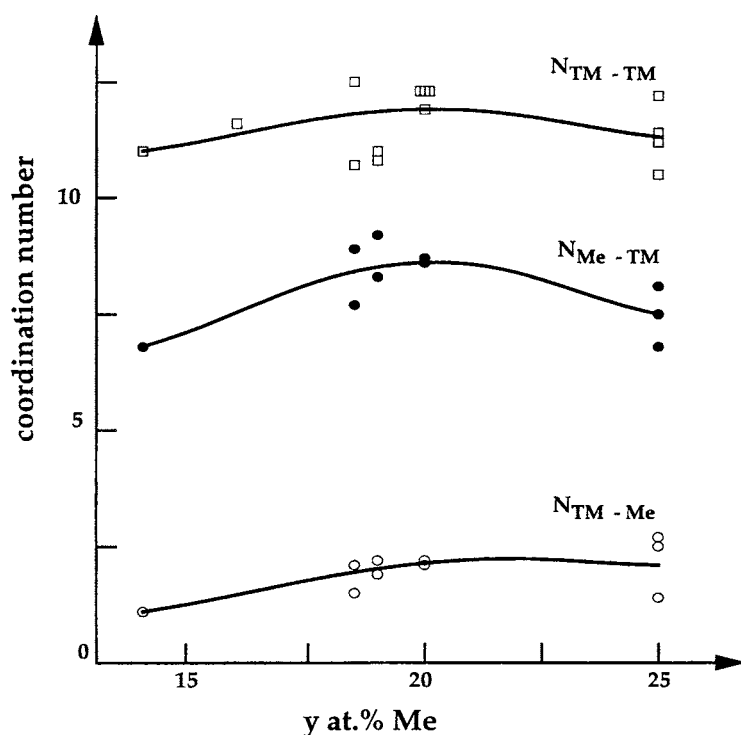
Figure 1. Experimental coordination numbers N_{TM-TM}, N_{Me-TM} and N_{TM-Me} in $TM_{100-y}Me_y$ amorphous alloys versus the y metalloid content [11–18].

drastic change of the local order was also detected by anomalous x-ray scattering (AWAXS) on amorphous $Co_{79-x-y}Er_xB_{21+y}$ at a critical concentration $x_c = 6$–7 at.% [8].

The aim of this paper is to explain the existence of this critical concentration x_c from a structural model issuing from local order of $TM_{100-y}Me_y$ and $TM_{100-z}RE_z$ amorphous alloys.

2. Local order in $TM_{100-y}Me_y$ amorphous alloys

The $TM_{100-y}Me_y$ amorphous alloys (TM = transition metal, Me = metalloid) are usually considered as built up of trigonal prismatic units [9, 10]. The most realistic atomic models are relaxed prismatic packing: either trigonal prismatic packing (TPP) (the Lennard-Jones interaction potentials used to relax the model are different according to the atomic pairs) or distorted prismatic packing (DPP) (a unique Lennard-Jones pair potential relaxes the atomic prismatic linkage). In the basic structural unit, the Me atom is surrounded by nine TM atoms as first neighbours and, in agreement with experimental structural results, these models exclude two first neighbours Me. For such an alloy with TM = Fe or Ni and Me = B and for several y Me contents ($14 < y < 25$), the coordination numbers N_{TM-TM}, N_{TM-Me} and N_{Me-TM} ($N_{Me-Me} = 0$) for each atomic species have been experimentally determined by x-ray or neutron diffraction, EXAFS and x-ray or neutron anomalous diffusion [11–18]. The data from the literature are reported in figure 1 as a function of the Me concentration. By interpolating the curves, these coordination numbers can be deduced for a given y metalloid content (table 1).

Table 1. Coordination numbers in TM$_{80-x}$RE$_x$Me$_{20}$ amorphous alloys which are considered as (TM$_{100-y}$Me$_y$)$_{20/y}$RE$_x$ type alloys: N_{TM-TM}, N_{TM-Me} and N_{Me-TM} are given for three x_{RE} contents and deduced by interpolation of the experimental curves which give the coordination numbers variations versus the y_{Me} content in TM_{100-y}Me$_y$ amorphous alloys (figure 1).

Coordination numbers	$x_{RE} = 4 \Rightarrow y_{Me} = 20.8$	$x_{RE} = 8 \Rightarrow y_{Me} = 21.7$	$x_{RE} = 12 \Rightarrow y_{Me} = 22.7$
N_{TM-TM}	12	12	12
N_{TM-Me}	2	2	2
N_{Me-TM}	8	8	8

B (2) : A$_5$B and A$_{17}$B$_2$ rhomb. and hex. (1st site) struct.

A (3) : A$_{17}$B$_2$ hex. struct.(2nd site)

B (2) : A$_5$B and A$_{17}$B$_2$ hex. struct. (1st site)

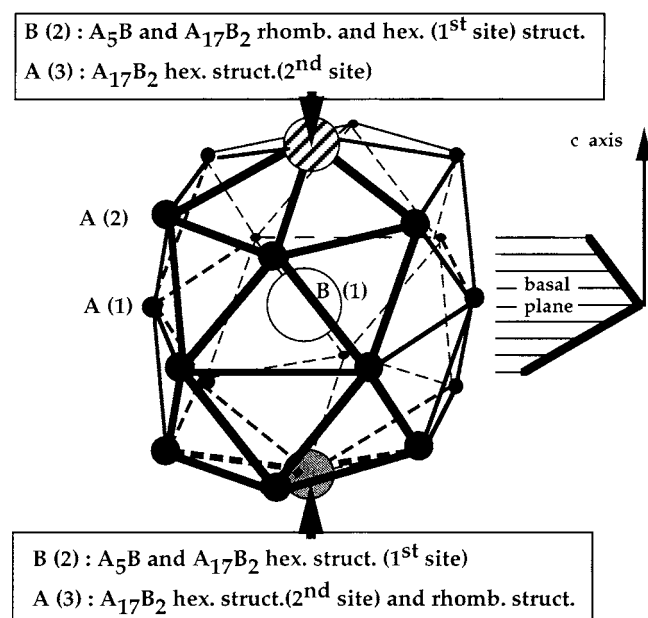**A (3) : A$_{17}$B$_2$ hex. struct.(2nd site) and rhomb. struct.**

Figure 2. First coordination shell around the B atoms (B = Y, Zr, Dy, ...) in A$_5$B, A$_{17}$B$_2$ hexagonal and A$_{17}$B$_2$ rhombohedral structures (A = Fe, Co, Ni, Cu, ...).

3. Local order in TM$_{100-z}$RE$_z$ crystallized or amorphous alloys

Crystallized and amorphous TM$_{100-z}$RE$_z$ systems, which contain small A atoms (A = Fe, Co, Ni, Cu, ...) and large B atoms (B = Y, Zr, Dy, ...) have been compared and have been proved to belong to the same structural group of A$_{100-z}$B$_z$ alloys [19]. For all these alloys, the ratio R_A/R_B of atomic radii corresponds to that of Laves phases A$_2$B. For some of these systems, Haucke phases A$_5$B (CaCu$_5$-like) exist, in which the large atom is 20 coordinated. A$_{17}$B$_2$ compounds are generally the first ones to crystallize on the A-rich side in the A–B binary diagrams and they are derived from A$_5$B compounds by the ordered substitution of each third B atom in the basal plane with a pair of A atoms [20]. The substituted layer may be stacked, either in the sequence abcabc . . . (rhombohedral Zn$_{17}$Th$_2$ type structure) or in the sequence abab . . . (hexagonal Ni$_{17}$Th$_2$ type structure). In the A$_5$B structure, the large B atoms have a triangulated coordination shell of 18 A and two B atoms, while A$_{17}$B$_2$ hexagonal structure exhibits two types of B site in equal quantity: the first one is built up of 18 A and two B atoms, and the second one of 20 A atoms around the B atoms. In the A$_{17}$B$_2$ rhombohedral structure, there is a unique site, constituted of 19 A and one B atoms as first neighbours of each B atom (figure 2).

The crystalline $A_{100-z}B_z$ alloys, i.e. $(Fe, Co, Ni, Cu, \ldots)_{100-z}(Y, Zr, Dy, \ldots)_z$ alloys, are generally of Franck and Kasper type [20]. They seem to retain the same local coordination in the amorphous state [19, 21]. Moreover, Machizaud *et al* [19] have shown a coherent dependence of the coordination numbers N_{A-A}, N_{A-B}, N_{B-A} and N_{B-B} upon the B content. As a result of that coherent dependence, which is observed for various amorphous or crystalline $A_{100-z}B_z$ alloys, all the coordination numbers may be determined for a given composition by interpolating the N_{A-A}, N_{A-B}, N_{B-A} and N_{B-B} curves versus the B content [19].

The A-rich amorphous $A_{100-z}B_z$ alloys are considered as dilute solutions of B atoms (i.e. Y or Zr, Dy, ...) in amorphous networks of pure A atoms (i.e. Fe or Co, Ni, Cu, ...), the structure of which is said to be 'polytetrahedral compact (PTC) structure' and characterized by an icosahedral local order [19, 22]. The N_{B-A} coordination number value extrapolated to ≈ 0 at.% B is found to be ≈ 20 [19]. This result indicates that the B atoms would be surrounded by ≈ 20 A atoms in very dilute solutions of glass forming B atoms as observed in fact around the B sites in crystalline $A_{17}B_2$ alloys (figure 2). The icosahedral local order of the PTC atomic structure is strongly induced by the existence of pentagonal rings of A atoms (centred on each A(2)-type atom) and of a pseudo 5-axis (along the B(1)A(2) type directions) that are clearly observed in the first coordination shell of B atoms (figure 2).

4. Local order in $TM_{80-x}RE_xMe_{20}$ amorphous alloys: structural model of $Fe_{80-x}RE_xB_{20}$ amorphous alloys ($0 < x \leqslant 16$)

To discuss the local order, we will compare experimental results with what would be expected, in two limit cases: either the local chemical order is imposed by the Me atoms or it is imposed by the RE atoms.

4.1. The metalloid dependence of the local atomic order is preponderant

If the local chemical order is imposed by the Me atoms, the Me atoms must be surrounded by TM atoms exclusively. This case should be observed at low RE content. The mean local order will be that of $TM_{100-y}Me_y$ amorphous alloys, i.e. that of a distorted prismatic packing. We can then consider a $TM_{80-x}RE_xMe_{20}$ amorphous alloy as a dilute solution of RE atoms in a $(TM_{100-y}Me_y)$ distorted prismatic network that will be labelled $(TM_{80-x}Me_{20})RE_x$ or $(TM_{100-y}Me_y)_{20/y}RE_x$ where $y = 100 \times (20/(100 - x))$. Consequently, the coordination numbers N_{TM-TM}, N_{TM-Me} and N_{Me-TM} of such an alloy may be determined from curves of figure 1 for a chosen y_{Me} content. The data are reported in table 1 for three y_{Me} contents corresponding to three x_{RE} compositions.

4.2. The rare earth dependence of the local atomic order is preponderant

If the local chemical order is imposed by the RE atoms (this case should be observed at high RE content), the RE atoms induce preferentially their first atomic coordination shell and the predominant local order will be similar to the icosahedral one characteristic of the $TM_{100-z}RE_z$ amorphous alloys, i.e. of the PTC structure. As a consequence, a $TM_{80-x}RE_xMe_{20}$ amorphous alloy will be viewed as a $(TM_{80-x}RE_x)Me_{20}$ or a $(TM_{100-z}RE_z)_{0.8}Me_{20}$ type alloy and considered as a dilute solution of RE atoms in a PTC network of TM atoms containing Me atoms as interstitial ones. As previously, the coordination numbers N_{TM-TM}, N_{TM-RE}, N_{RE-TM} and N_{RE-RE} can be deduced from figures 3 and 4, which give the variations of the coordination numbers versus the z_{RE} content in $TM_{100-z}RE_z$ alloys [19].

Table 2 brings together the data for three $x_{RE}(\Rightarrow z_{RE})$ contents.
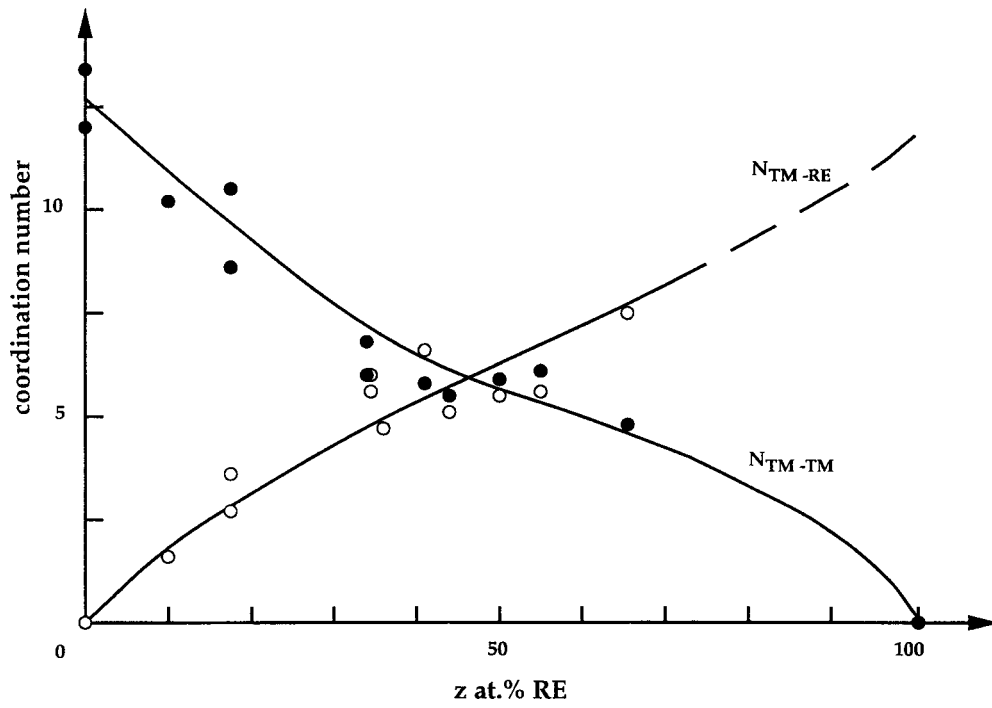
Figure 3. Experimental coordination numbers N_{TM-TM} and N_{TM-RE} in TM$_{100-z}$RE$_z$ alloys versus the z rare earth content [19].
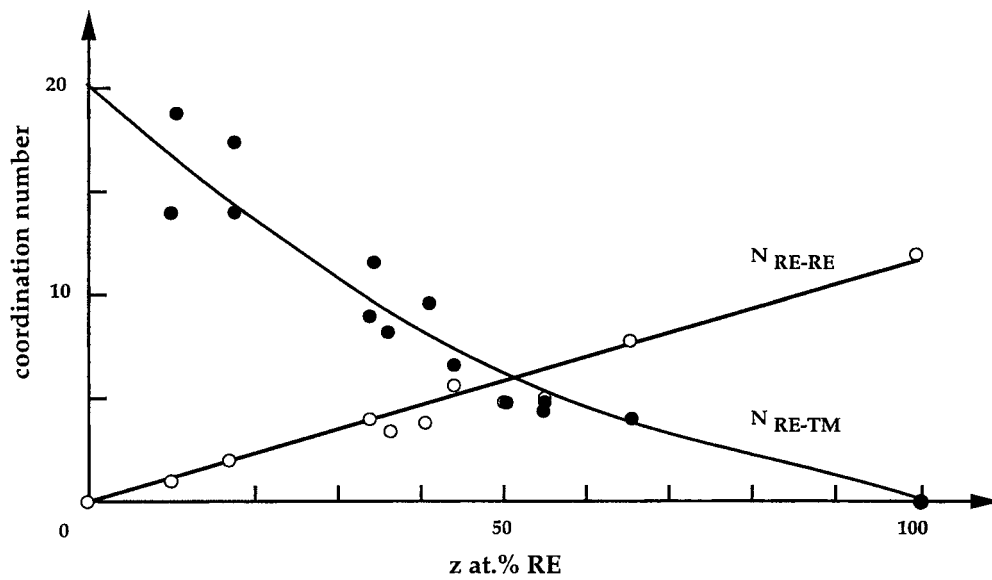

Figure 4. Experimental coordination numbers N_{RE-TM} and N_{RE-RE} in TM$_{100-z}$RE$_z$ alloys versus the z rare earth content [19].

Table 2. Coordination numbers in $TM_{80-x}RE_xMe_{20}$ amorphous alloys which are considered as $(TM_{100-z}RE_z)_{0.8}Me_{20}$ type alloys: N_{TM-TM}, N_{TM-RE}, N_{RE-TM} and N_{RE-RE} are given for three x_{RE} contents and deduced by interpolation of the experimental curves which give the coordination number variations versus the z_{RE} content in $TM_{100-z}RE_z$ alloys.

Coordination numbers	$x_{RE} = 4 \Rightarrow z_{RE} = 5$	$x_{RE} = 8 \Rightarrow z_{RE} = 10$	$x_{RE} = 12 \Rightarrow z_{RE} = 15$
N_{TM-TM}	11	10	9
N_{TM-RE}	1	2	3
N_{RE-TM}	18	17	15
N_{RE-RE}	0.6	1	2

Table 3. Contributions (%) of atomic pairs TM–TM, TM–Me and Me–TM as a function of the x_{RE} content in $(Fe_{80-x}B_{20})RE_x$ amorphous alloys, considered as $(TM_{100-y}Me_y)_{20/y}RE_x$ type alloys.

	$x_{RE} = 4$	$x_{RE} = 8$	$x_{RE} = 12$
TM–TM (%)	74	73	73
TM–Me (%)	13	13	13
Me–TM (%)	13	14	15

Table 4. Contributions (%) of atomic pairs TM–TM, TM–RE, RE–TM and RE–RE as a function of the x_{RE} content in $(Fe_{80-x}RE_x)B_{20}$ amorphous alloys, considered as $(TM_{100-z}RE_z)_{0.8}B_{20}$ type alloys.

	$x_{RE} = 4$	$x_{RE} = 8$	$x_{RE} = 12$
TM–TM (%)	85	73	64
TM–RE (%)	8	13	17
RE–TM (%)	7	14	18
RE–RE (%)	0.3	0.8	2

4.3. Structural model of $Fe_{80-x}RE_xB_{20}$ amorphous alloys (0 < x < 16)

$Fe_{80-x}RE_xB_{20}$ amorphous alloys being considered as $(TM_{100-y}Me_y)_{20/y}RE_x$ or $(TM_{100-z}RE_z)_{0.8}B_{20}$ type alloys, tables 1 or 2, and the knowledge of the atomic composition allow us to calculate the percentage of each atomic pair of bulk material (which is proportional to the element concentration multiplied by its coordination number). The deduced data are reported in tables 3 and 4 respectively. As expected, it is noteworthy that the calculated number of atomic pairs TM–Me and Me–TM are almost identical and likewise concerning atomic pairs TM–RE and RE–TM, which justifies all together the interpolated data of tables 1 and 2 and the calculated atomic pair contributions of tables 3 and 4.

In figure 5, we plotted the contributions of (TM–Me, Me–TM) and (TM–RE, RE–TM) pairs versus the x_{RE} content. First, the intersection of the two sets of curves appears to be without ambiguity in a critical range of composition 7.7–9.2 at.%, which is very close to the critical concentration $x_c = 8$–9 at.% deduced from our previous Mössbauer study [5, 6]. Secondly, in the range of composition investigated, the set of (TM–Me, Me–TM) pairs remains almost constant while the set of (TM–RE, RE–TM) pairs increases with the RE content. So, we can explain the local order in the following way:

(a) *At low RE concentration*, the (TM–Me, Me–TM) pair contribution is more important than that of (TM–RE, RE–TM) pairs. Therefore we can assure that the metalloid atoms must impose the local atomic order which exists in $TM_{100-y}Me_y$ amorphous alloys, i.e. a trigonal or distorted prismatic packing. In our case, the structural units are constituted of

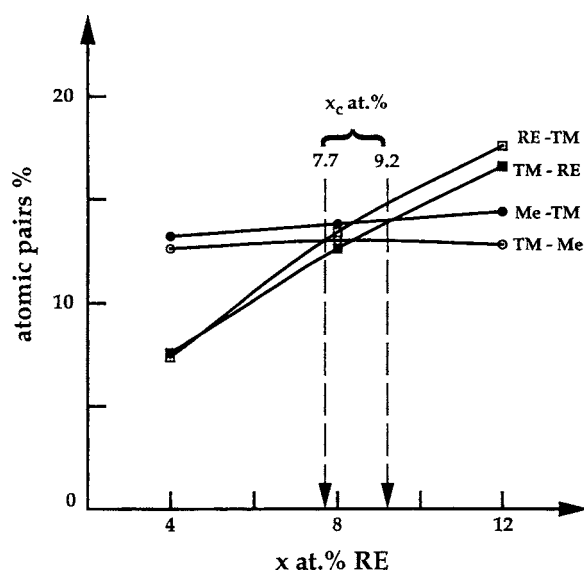**Figure 5.** Contributions (%) of the (TM–Me, Me–TM) and (TM–RE, RE–TM) atomic pairs in TM$_{80-x}$RE$_x$Me$_{20}$ amorphous alloys as a function of the RE content.

one boron atom surrounded by nine iron atoms. This agrees with the low RE Mossbauer data, for which extrapolated values at $x_{RE} = 0$ give values of binary Fe$_{80}$B$_{20}$ amorphous alloy. The negligible contribution of the RE atoms to the mean local order was noticed as well by AWAXS in Co$_{79-x-y}$Er$_x$B$_{21+y}$ amorphous ribbons where Er local segregation effects seem to occur at low Er content [8].

(b) *At high RE concentration* the increase of the (TM–RE, RE–TM) pair contribution indicates the RE atoms to be the most influential. Above the critical x_c concentration, AWAXS study on Co$_{79-x-y}$Er$_x$B$_{21+y}$ amorphous ribbons leads to the conclusion of structural units including the rare earth [8]. These results agree with the observed decreasing of the Fe magnetic moment in our alloys, which is correlated to an increasing hybridization of Fe 3d and RE 5d states [23–25]. Consequently, taking into account the atomic environment of the RE atom (figure 2), which exhibits atomic pentagonal rings and a pseudo 5-axis, the increase of the RE influence must originate from the peculiar icosahedral PTC structure of the TM$_{100-z}$RE$_z$ amorphous alloys. Then, the alloys may be viewed mainly as dilute solutions of RE atoms in an icosahedral network of TM atoms.

(c) *In the vicinity of the critical x_c concentration* and in order to validate the proposed structural model, two different local orders which are suggested below and above x_c respectively could coexist. Figures 6(a) and 6(b) explain how slight atomic displacements and distortions in the first coordination shell of the RE atoms make it possible for prismatic units to link with atomic sites of the RE and to coexist with TM icosahedral sites of the PTC network. Moreover, the great similarity between the distorted RE site which is linked with two prismatic units (figure 6(b)) and the prismatic linkage of the tetragonal TM$_3$Me structure (figures 6(c) and 6(d)) allows us to explain why the metastable t-Fe$_3$B boride may be the first one to precipitate upon crystallization. On heating of Fe$_{80-x}$RE$_x$B$_{20}$ amorphous alloys, we observed effectively that the presence of the rare earth atoms induces preferentially the crystallization of t-Fe$_3$B boride, which transforms into the stable o-Fe$_3$B boride at higher temperatures [6, 7].
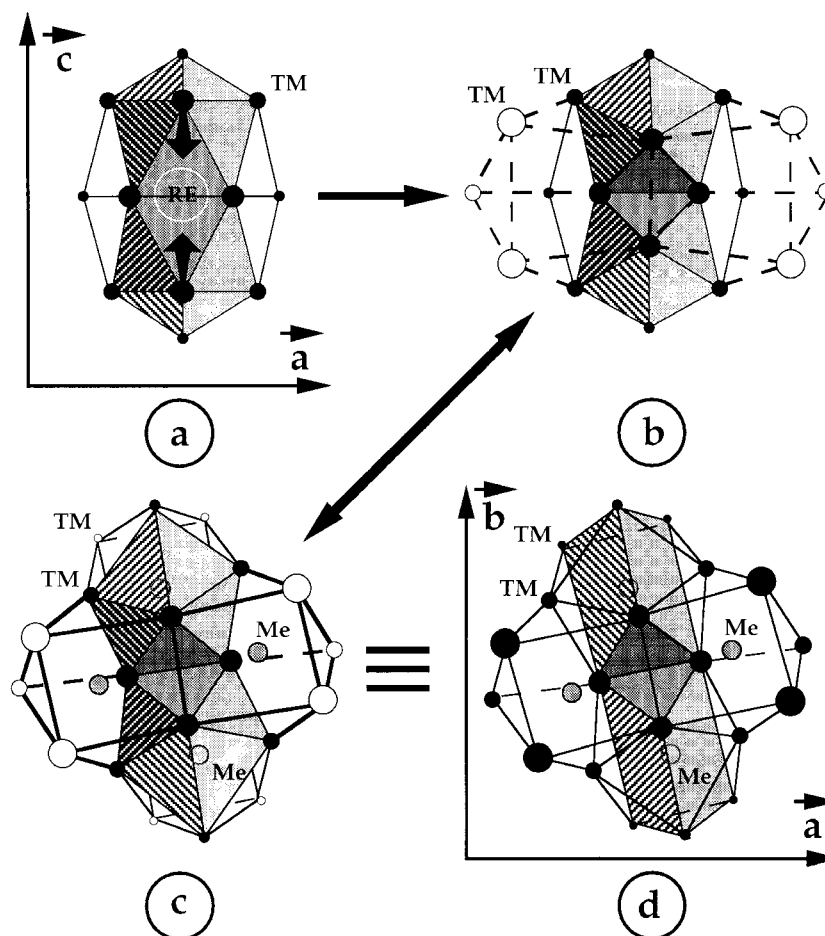
Figure 6. (a) 20-coordinated shell around RE atoms in $TM_{100-z}RE_z$ alloys (atomic cluster of figure 2 projected on the (010) plane of the $TM_{17}RE_2$ structure). The arrows indicate the atomic displacements which lead to the atomic configuration (b) and allow two prismatic units (dotted lines) to be linked. (c) and (d) are two representations of the same TM_3Me tetragonal structure, projection on the (001) plane.

5. Conclusion

We were able to explain the existence of a discontinuity in the local order around Fe atoms in $Fe_{80-x}RE_xB_{20}$ amorphous alloys at a critical concentration $x_c = 8$–9 at.%, evidenced by Mössbauer spectrometry. This discontinuity is interpreted in terms of a change in the structural local order, by considering two limit cases. Below x_c, $Fe_{80-x}RE_xB_{20}$ amorphous alloys can be considered as a dilute solution of RE atoms in a $(TM_{100-y}Me_y)$ distorted prismatic network. Above x_c, they can be considered as dilute solutions of RE atoms in a polytetrahedral compact network of TM atoms containing Me atoms as interstitial ones. The comparison of the calculated atomic pairs with previous experimental results in these two cases provides evidence for x_c around 8.5 at.%.

References

[1] Hansen P 1991 *Handbook of Magnetic Materials* vol 6, ed K H J Buschow (Amsterdam: North-Holland–Elsevier) pp 289–452

[2] Bara J J, Bogacz B F, Idzikowski B, Pedziwiatr A T and Wrzeciono A 1994 *J. Magn. Magn. Mater.* **131** 333

[3] Filoti G, Kuncser V, Serbanescu M D, Jianu A, Cristea L, Noguès M, Dormann J L and Maknani J 1993 *IEEE Trans. Magn.* **29** 3123

[4] Ravach G, Fnidiki A, Teillet J, Grenèche J M, Krishnan R and Lassri H 1996 *J. Magn. Magn. Mater.* **140–144** 317–18

[5] Ravach G, Teillet J, Fnidiki A, Le Breton J M, Driouch L and Hassanaïn N 1996 *J. Magn. Magn. Mater.* **157/158** 173

[6] Ravach G 1997 *Thesis* Université de Rouen

[7] Ravach G, Machizaud F, Teillet J, Le Breton J M and Fnidiki A 2000 *J. Phys.: Condens. Matter* **12** 3639

[8] Bouchet-Fabre B, Kebab A, Dixmier J, Lassri H and Krishnan R 1995 *J. Non Cryst. Solids* **192–193** 355

[9] Gaskell P H 1979 *J. Non-Cryst. Solids* **32** 207

[10] Gaskell P H 1981 *Nature* **289** 474

[11] Waseda Y and Chen H S 1978 *Phys. Status Solidi* a **49** 387

[12] Waseda Y 1978 *Proc. 3rd Int. Conf. on Rapidly Quenched Metals* vol 2 (London: Metals Society) p 352

[13] Aur S, Egami T and Vincze I 1981 *Proc. 4th Int. Conf. on Rapidly Quenched Metals (Sendaï, 1981)* ed T Masumoto (Japan Institute of Metals) p 351

[14] Lamparter P, Sperl W, Nold E, Rainer-Harbach G and Steeb S 1981 *Proc. 4th Int. Conf. on Rapidly Quenched Metals (Sendaï, 1981)* ed T Masumoto (Japan Institute of Metals) p 343

[15] Lamparter P, Nold E, Rainer-Harbach G, Grallath E and Steeb S 1981 *Z. Naturf.* a **36** 165

[16] Nold E, Lamparter P, Olbrich H, Rainer-Harbach G and Steeb S 1981 *Z. Naturf.* a **36** 1032

[17] Swanson H E *et al* 1955 *NBS Circular 539* vol IV, 3

[18] Matz W, Hermann H and Mattern N 1987 *J. Non-Cryst. Solids* **93** 217

[19] Machizaud F, Laridjani M, Du Trémolet De Lacheisserie E 1990 *J. Magn. Magn. Mater.* **92** 207

[20] Franck F C and Kasper J S 1959 *Acta Crystallogr.* **12** 483

[21] Laridjani M and Sadoc J F 1989 *J. Physique* **50** 1953

[22] Laridjani M and Sadoc J F 1988 *Int. J. Mod. Phys.* B **2** 37

[23] Hassanain N, Lassri M, Krishnan R and Berrada A 1995 *J. Magn. Magn. Mater.* **146** 37

[24] Radwanski R J, Krishnan R, Franse J J M, Lassri H and El Marrekchi O 1993 *Int. J. Mod. Phys.* B **7** 950

[25] Driouch L 1995 *Thesis* Université de Rouen