Valence transition of samarium in hexaboride solid solutions Sm 1-xMxB6 (M = Yb 2+ , Sr2+ , La3+ , Y3+ , Th4+)

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Valence transition of samarium in hexaboride solid solutions Sm$_{1-x}$M$_x$B$_6$ (M = Yb^{2+}, Sr^{2+}, La^{3+}, Y^{3+}, Th^{4+})

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Résumé. — Des mesures d'absorption X (seuil L$_{III}$ du samarium) ont été effectuées à 300 K sur les solutions solides Sm$_{1-x}$M$_x$B$_6$ (M = Yb^{2+}, Sr^{2+}, La^{3+}, Y^{3+}, Th^{4+}). Lorsque *x* croît la variation des intensités des pics correspondant au seuil L$_{III}$ des configurations Sm^{2+} : 4f^6 et Sm^{3+} : 4f^5 indique que le degré d'oxydation moyen du samarium tend vers 3 avec Yb^{2+} et Sr^{2+} alors qu'il tend vers 2 avec La^{3+}, Y^{3+} et Th^{4+}. Les résultats obtenus sont confirmés par les mesures de susceptibilité magnétique et de paramètre cristallin.

Abstract. — The X-ray absorption measurements at the L$_{III}$ edge have been carried out at 300 K in the solid solutions Sm$_{1-x}$M$_x$B$_6$ (M = Yb^{2+}, Sr^{2+}, La^{3+}, Y^{3+}, Th^{4+}). The fine structure of the edge indicates that the average samarium valence tends towards Sm^{3+} with increasing Yb^{2+} and Sr^{2+} contents whereas the substitutions with La^{3+}, Y^{3+} and Th^{4+} involve a decrease of the average samarium valence reaching Sm^{2+} as *x* increases. The entire results obtained agree well with those deduced from the analysis of the cubic lattice parameter variation and from the magnetic susceptibility measurements.

SmB$_6$ is of interest because it is one of a group of mixed configuration compounds in which there is non integer occupation of the rare earth ion 4f shell. Thus, SmB$_6$ is a homogeneous mixed-valence compound having 4f localized states hybridized with broad 5de$_g$ conduction band states. Experimental results indicate that the ratio Sm^{2+} : Sm^{3+} is about 4 : 6 at 300 K [1, 2].

We looked for reasons which might change the average samarium valence in SmB$_6$. Two kinds of substitution seemed interesting to study : 1) the influence of samarium substitution by non magnetic divalent atoms (Yb^{2+}, Sr^{2+}) which play a dilution role and reduce the number of conduction electrons in the 5de$_g$ conduction band, 2) the influence of samarium substitution by non magnetic trivalent or tetravalent cations (La^{3+}, Y^{3+}, Th^{4+}) which have a dilution role and introduce conduction electrons in the 5de$_g$ band (1e$^-$ per La^{3+} or Y^{3+} cation, 2e$^-$ per Th^{4+} cation) [3, 4].

In a previous paper, we showed, from lattice parameter and magnetic measurements that the substi-

tution of Sm by Yb^{2+} in SmB$_6$ increases the average samarium valence whereas the opposite effect is observed with La^{3+} substitution [5].

The present work will show that X-ray absorption measurement is a powerful method for giving direct evidence of the samarium valence change in the Sm$_{1-x}$M$_x$B$_6$ systems (M = Yb^{2+}, Sr^{2+}, La^{3+}, Y^{3+}, Th^{4+}). The results obtained will be compared with those deduced from the analysis of the cubic lattice parameter variation as a function of *x* and from magnetic susceptibility measurements.

1. Experimental. — The solid solutions Sm$_{1-x}$M$_x$B$_6$ (M = Yb^{2+}, Sr^{2+}, La^{3+}, Y^{3+}, Th^{4+}) have been prepared by borothermic reduction of the corresponding oxides under vacuum at high temperature, according to a method described previously. The exact values of *x* have been determined by X-ray fluorescence analysis and checked by density measurements [5].

The cubic lattice parameters have been determined by an extrapolation method from Debye-Scherrer spectra at room temperature.

The X-ray absorption experiments have been

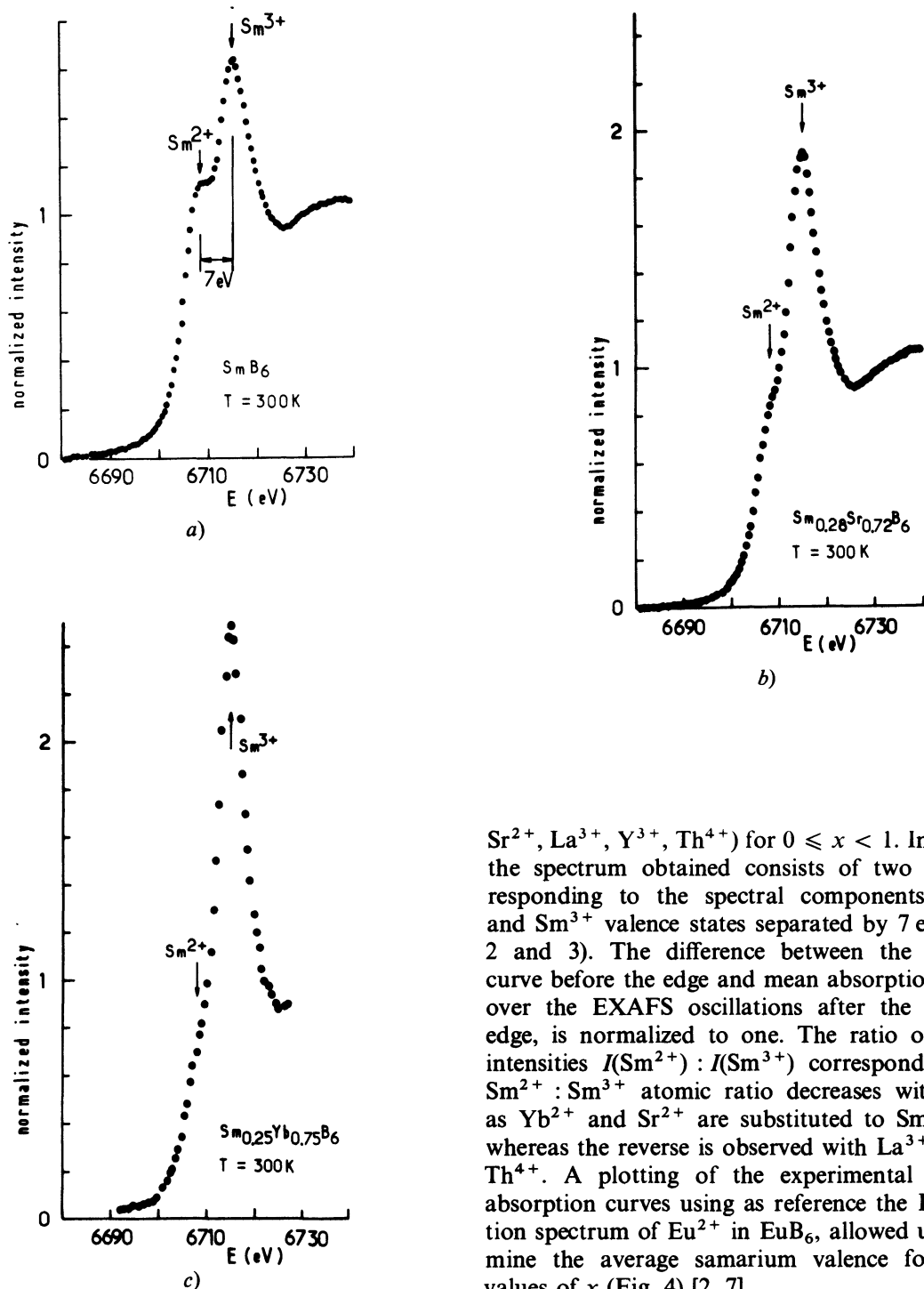(*) Department of Physics, Faculty of Science, Tohoku University, Sendai, Japan.

Fig. 1. — L_{III} absorption edge at 300 K in : *a*) SmB$_6$; *b*) Sm$_{0.28}$Sr$_{0.72}$B$_6$; *c*) Sm$_{0.25}$Yb$_{0.75}$B$_6$.

carried out with the synchrotron at Orsay-France (LURE). The X-ray beam is emitted by 1.72 GeV electrons in the ring D.C.I. More details are given in references [2] and [6].

2. **Results and discussion.** — The X-ray absorption measurements at the L_{III} edge have been performed at 300 K for the Sm$_{1-x}$M$_x$B$_6$ systems (M = Yb^{2+},

Sr^{2+}, La^{3+}, Y^{3+}, Th^{4+}) for $0 \leqslant x < 1$. In each case, the spectrum obtained consists of two peaks corresponding to the spectral components of Sm^{2+} and Sm^{3+} valence states separated by 7 eV (Figs. 1, 2 and 3). The difference between the absorption curve before the edge and mean absorption averaged over the EXAFS oscillations after the absorption edge, is normalized to one. The ratio of the peak intensities $I(Sm^{2+})$: $I(Sm^{3+})$ corresponding to the Sm^{2+} : Sm^{3+} atomic ratio decreases with rising x as Yb^{2+} and Sr^{2+} are substituted to Sm in SmB$_6$, whereas the reverse is observed with La^{3+}, Y^{3+} and Th^{4+}. A plotting of the experimental L_{III} X-ray absorption curves using as reference the L_{III} absorption spectrum of Eu^{2+} in EuB$_6$, allowed us to determine the average samarium valence for different values of x (Fig. 4) [2, 7].

The magnetic susceptibility measurements performed between 300 K and 4.2 K are summarized in figure 5. The susceptibilities χ have been corrected by subtraction of the susceptibility of the diamagnetic hexaborides (YbB$_6$, SrB$_6$, LaB$_6$, YB$_6$, ThB$_6$) [4, 5]. The data are consistent with the samarium valence change, as a function of x, found above by X-ray absorption. At room temperature the magnetic susceptibility has a value intermediate between those of the free Sm^{2+} and Sm^{3+} cations. It can be described approximately at 300 K by :
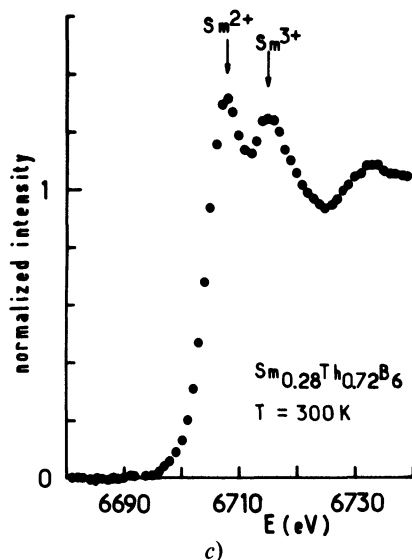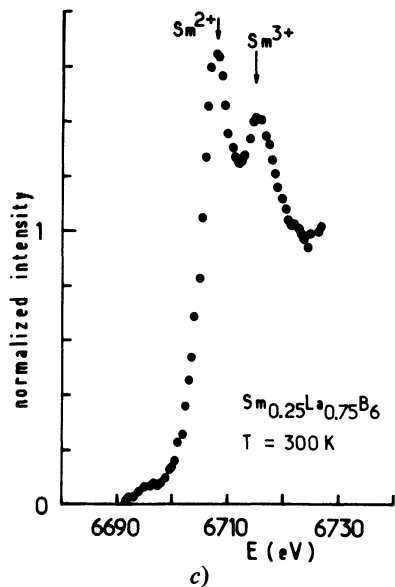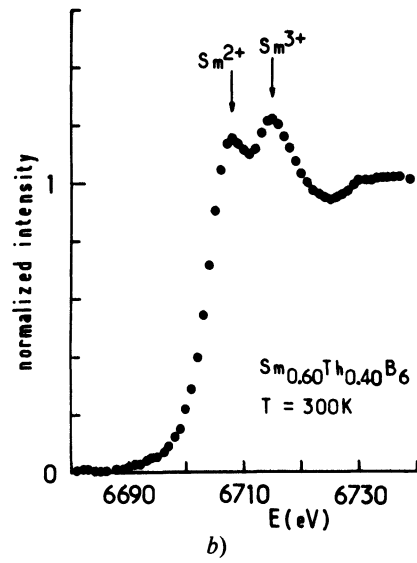
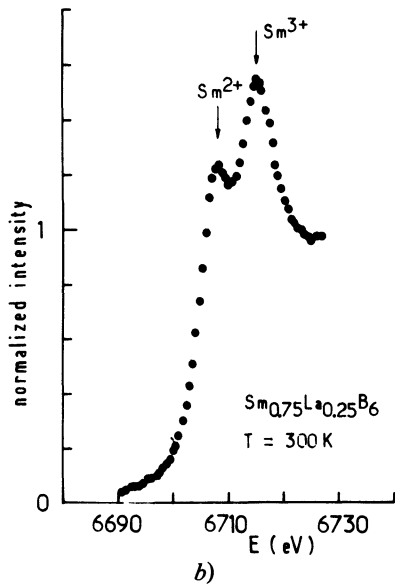$$\chi = z\chi_{Sm^{3+}} + (1 - z)\,\chi_{Sm^{2+}}$$
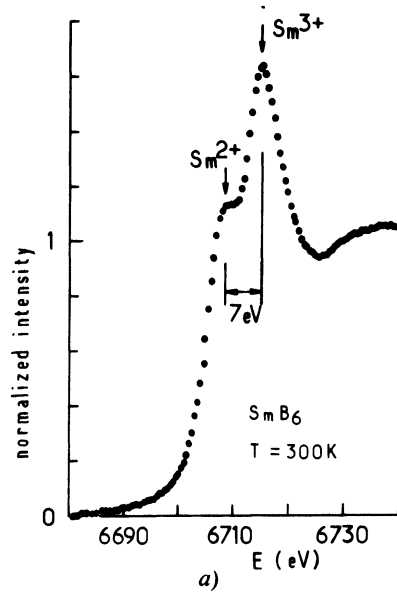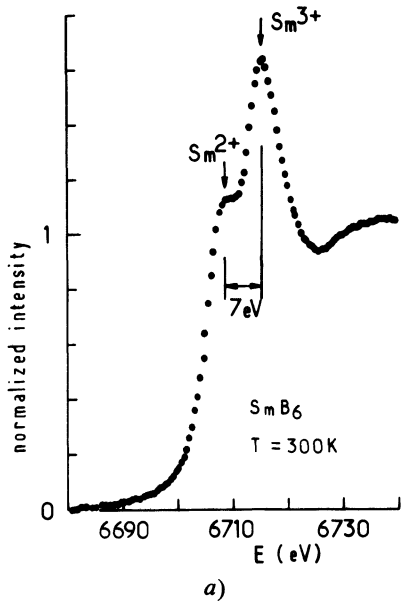
Fig. 2. — L_{III} absorption edge at 300 K in : a) SmB_6 ; b) $Sm_{0.75}La_{0.25}B_6$; c) $Sm_{0.25}La_{0.75}B_6$.

Fig. 3. — L_{III} absorption edge at 300 K in : a) SmB_6 ; b) $Sm_{0.60}Th_{0.40}B_6$; c) $Sm_{0.28}Th_{0.72}B_6$.
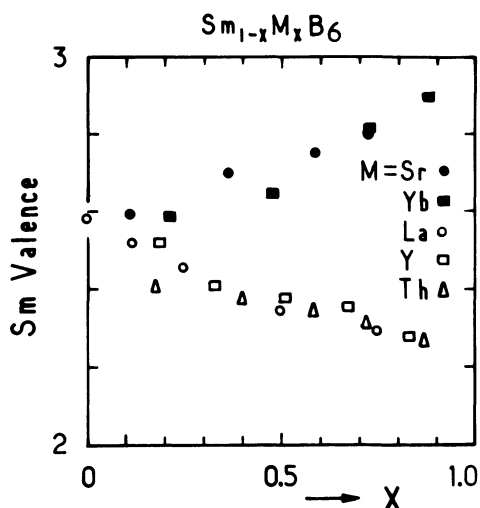
Fig. 4. — Average samarium valence determined from X-ray absorption measurements in the $Sm_{1-x}M_xB_6$ systems ($M = Yb^{2+}$, Sr^{2+}, Y^{3+}, La^{3+}, Th^{4+}).

b)
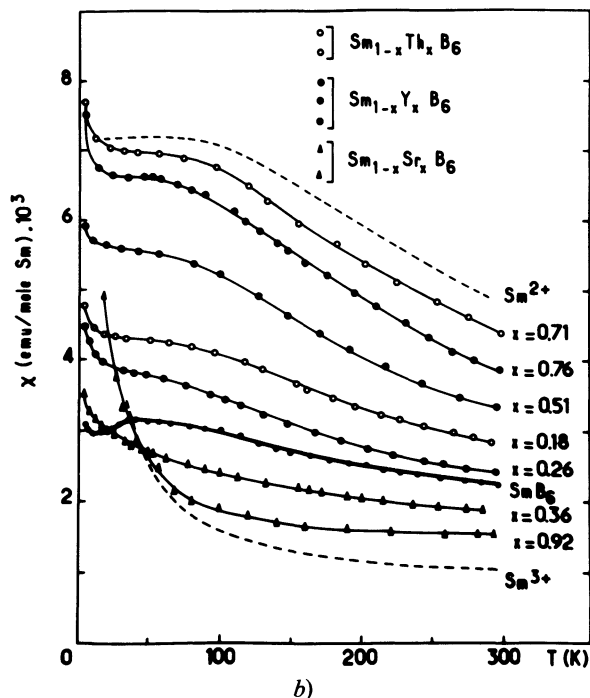
Fig. 5. — Magnetic susceptibility per mole of Sm as a function of temperature : *a)* $Sm_{1-x}Yb_xB_6$ and $Sm_{1-x}La_xB_6$; *b)* $Sm_{1-x}Sr_xB_6$, $Sm_{1-x}Y_xB_6$ and $Sm_{1-x}Th_xB_6$.

a)
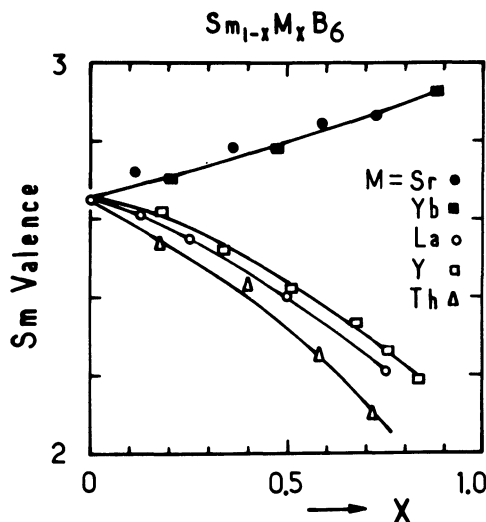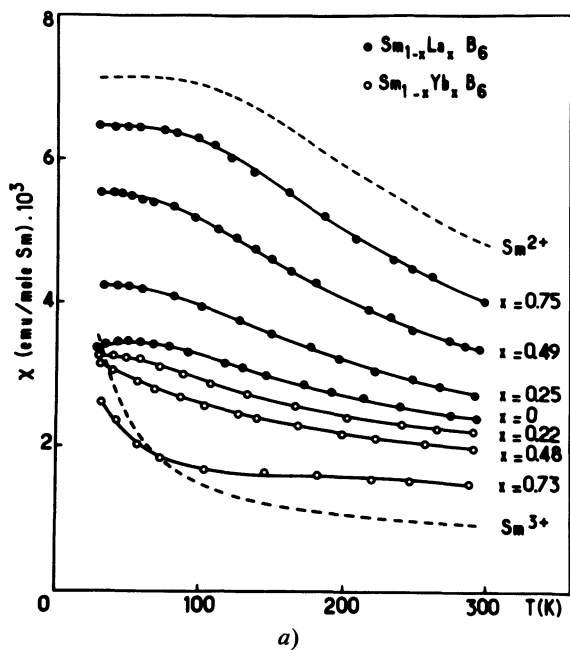

Fig. 6. — Average samarium valence determined from magnetic susceptibility measurements at 300 K in the $Sm_{1-x}M_xB_6$ systems ($M = Yb^{2+}$, Sr^{2+}, Y^{3+}, La^{3+}, Th^{4+}).

where $\chi_{Sm^{3+}}$ and $\chi_{Sm^{2+}}$ have been calculated using the spin-orbit parameters of 420 K and 500 K for Sm^{2+} and Sm^{3+} respectively. The average valence of Sm in the solid solutions is given by $2 + z$ (Fig. 6). The variation of the average samarium valence, as a function of x, is approximately the same for both $Sm_{1-x}Yb_xB_6$ and $Sm_{1-x}Sr_xB_6$ systems ; a similar remark can be made with the $Sm_{1-x}La_xB_6$ and $Sm_{1-x}Y_xB_6$ systems. Let us note that the average samarium valence with $M = Th^{4+}$ decreases more rapidly than with $M = La^{3+}$ and Y^{3+}.

The variation of the cubic lattice parameter of the $Sm_{1-x}M_xB_6$ systems as a function of x is not linear

(Fig. 7). The deviation from Vegard's law is due to the change of the samarium valence state (ionic radius : $r_{Sm^{2+}} > r_{Sm^{3+}}$) but also to the presence of conduction electrons which tend to shrink the metal-metal bonding, involving a decrease of the volume of the unit cell.

We have attempted to estimate the variation of the average samarium valence as a function of x from the lattice parameter in the hexaborides

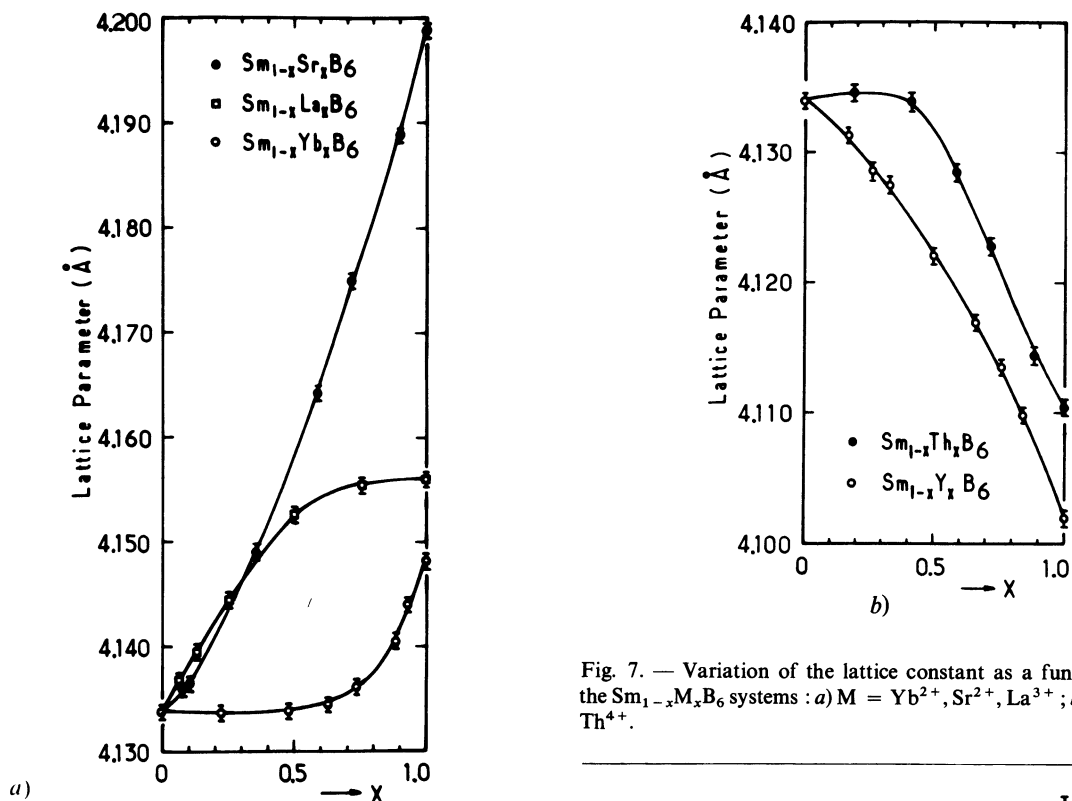$$(Sm_{1-y}^{2+}Sm_y^{3+})_{1-x}M_xB_6 \ .$$

Fig. 7. — Variation of the lattice constant as a function of x in the $Sm_{1-x}M_xB_6$ systems : $a)$ M = $Yb^{2+}, Sr^{2+}, La^{3+}$; $b)$ M = Y^{3+}, Th^{4+}.
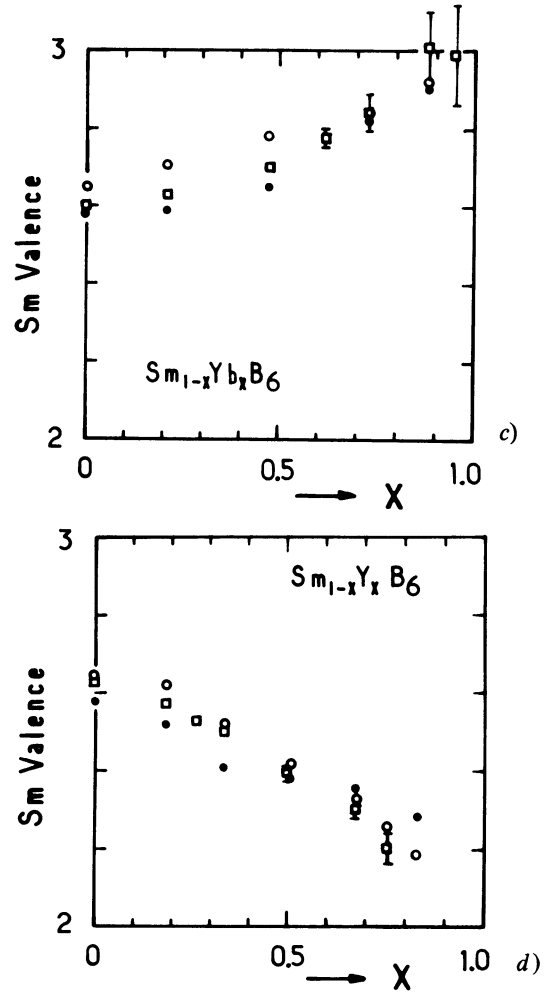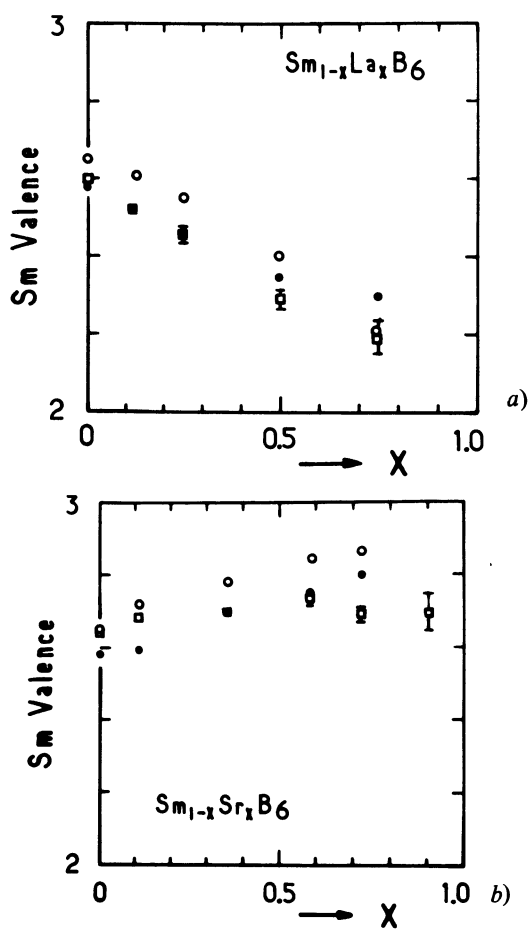

Fig. 8. — Average samarium valence at 300 K in the $Sm_{1-x}M_xB_6$ systems. Comparison of the results given by different methods. ● (black circles) X-ray absorption ; O (open circles) magnetic susceptibility ; □ (open squares) lattice parameter variation. $a)$ M = La^{3+} ; $b)$ M = Sr^{2+} ; $c)$ M = Yb^{2+} ; $d)$ M = Y^{3+}.

These compounds can be considered as solid solutions between the hypothetical hexaborides $Sm_{1-x}^{2+}M_xB_6$ and $Sm_{1-x}^{3+}M_xB_6$ which are themselves solid solutions between MB_6 and « $Sm^{2+}B_6$ » or « $Sm^{3+}B_6$ » respectively. The lattice parameter of pure divalent ($a = 4.186$ Å) and pure trivalent ($a = 4.115$ Å) SmB_6 have been interpolated from those of neighbouring divalent and trivalent rare earth hexaborides. The contribution to the Vegard's law due to conduction electrons has been estimated from the variation of the lattice parameter of $Eu_{1-x}^{2+}La_x^{3+}B_6$, $Eu_{1-x}^{2+}Gd_x^{3+}B_6$ and $Eu_{1-x}^{2+}Y_x^{3+}B_6$ systems [3]. This method gives results in good agreement with those deduced from X-ray absorption and magnetic susceptibility measurements for the $Sm_{1-x}Yb_x^{2+}B_6$, $Sm_{1-x}La_x^{3+}B_6$ and $Sm_{1-x}Y_x^{3+}B_6$ systems. The method is valid only for concentrations less than $x \simeq 0.5$ in the $Sm_{1-x}Sr_xB_6$ system (Fig. 8).

SmB_6 is considered as being a homogeneous mixed-valent compound with occupied and unoccupied 4f levels pinned at the Fermi level. It has been shown from the above experiments (X-ray absorption, magnetic susceptibility and lattice parameter) that the hexaborides $Sm_{1-x}M_xB_6$ ($M = Yb^{2+}$, Sr^{2+}, La^{3+}, Y^{3+}, Th^{4+}) are mixed valent compounds for $0 \leqslant x < 1$. The decrease of the $Sm^{2+} : Sm^{3+}$ ratio as x increases in

$$Sm_{1-x}Yb_x^{2+}B_6 \quad \text{and} \quad Sm_{1-x}Sr_x^{2+}B_6$$
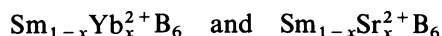
hexaborides suggests that the 4f levels, and therefore the Fermi level are lowered with respect to the bottom of the $5de_g$ conduction band. The samarium substitution by La^{3+} and Y^{3+} in SmB_6 introduces one electron per cation in the conduction band, whereas the substitution by Th^{4+} introduces two electrons [4]. Thus, as x increases, we must expect, the Fermi level to rise with respect to the bottom of the conduction band, involving the formation of Sm^{2+} by electron localization ($Sm^{3+} + e^- \rightarrow Sm^{2+}$).

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