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

Jean-marie Tarascon, Y. Isikawa, Bernard Chevalier, Jean Etourneau, Paul Hagenmuller, M. Kasaya

► To cite this version:

Jean-marie Tarascon, Y. Isikawa, Bernard Chevalier, Jean Etourneau, Paul Hagenmuller, et al.. Valence transition of samarium in hexaboride solid solutions $\text{Sm}_{1-x}\text{MxB}_6$ ($\text{M} = \text{Yb}^{2+}$, Sr^{2+} , La^{3+} , Y^{3+} , Th^{4+}). Journal de Physique, 1980, 41 (10), pp.1135-1140. 10.1051/jphys:0198000410100113500 . jpa-00208939

HAL Id: jpa-00208939

<https://hal.science/jpa-00208939>

Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
Physics Abstracts
78.70D

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

J. M. Tarasçon, Y. Isikawa (*), B. Chevalier, J. Etourneau, P. Hagenmuller

Laboratoire de Chimie du Solide du C.N.R.S., Université de Bordeaux I,
351, cours de la Libération, 33405 Talence Cedex, France

and M. Kasaya

Department of Physics, Faculty of Science, Tohoku University, Sendai, Japan

(Reçu le 18 mars 1980, accepté le 29 mai 1980)

Résumé. — Des mesures d'absorption X (seuil L_{III} du samarium) ont été effectuées à 300 K sur les solutions solides $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ ($\text{M} = \text{Yb}^{2+}, \text{Sr}^{2+}, \text{La}^{3+}, \text{Y}^{3+}, \text{Th}^{4+}$). Lorsque x croît la variation des intensités des pics correspondant au seuil L_{III} des configurations $\text{Sm}^{2+} : 4f^6$ et $\text{Sm}^{3+} : 4f^5$ 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 $\text{La}^{3+}, \text{Y}^{3+}$ 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 $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ ($\text{M} = \text{Yb}^{2+}, \text{Sr}^{2+}, \text{La}^{3+}, \text{Y}^{3+}, \text{Th}^{4+}$). 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 $\text{La}^{3+}, \text{Y}^{3+}$ 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 $5d_e$ conduction band states. Experimental results indicate that the ratio $\text{Sm}^{2+} : \text{Sm}^{3+}$ 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 ($\text{Yb}^{2+}, \text{Sr}^{2+}$) which play a dilution role and reduce the number of conduction electrons in the $5d_e$ conduction band, 2) the influence of samarium substitution by non magnetic trivalent or tetravalent cations ($\text{La}^{3+}, \text{Y}^{3+}, \text{Th}^{4+}$) which have a dilution role and introduce conduction electrons in the $5d_e$ 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 $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ systems ($\text{M} = \text{Yb}^{2+}, \text{Sr}^{2+}, \text{La}^{3+}, \text{Y}^{3+}, \text{Th}^{4+}$). 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 $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ ($\text{M} = \text{Yb}^{2+}, \text{Sr}^{2+}, \text{La}^{3+}, \text{Y}^{3+}, \text{Th}^{4+}$) 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 $Sm_{1-x}M_xB_6$ systems ($M = Yb^{2+}$,

Sr^{2+} , La^{3+} , Y^{3+} , Th^{4+}) for $0 \leq x < 1$. 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) $\text{Sm}_{0.75}\text{La}_{0.25}\text{B}_6$; c) $\text{Sm}_{0.25}\text{La}_{0.75}\text{B}_6$.

Fig. 3. — L_{III} absorption edge at 300 K in : a) SmB_6 ; b) $\text{Sm}_{0.60}\text{Th}_{0.40}\text{B}_6$; c) $\text{Sm}_{0.28}\text{Th}_{0.72}\text{B}_6$.

Fig. 4. — Average samarium valence determined from X-ray absorption measurements in the $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ systems ($M = \text{Yb}^{2+}$, Sr^{2+} , Y^{3+} , La^{3+} , Th^{4+}).

Fig. 5. — Magnetic susceptibility per mole of Sm as a function of temperature : a) $\text{Sm}_{1-x}\text{Yb}_x\text{B}_6$ and $\text{Sm}_{1-x}\text{La}_x\text{B}_6$; b) $\text{Sm}_{1-x}\text{Sr}_x\text{B}_6$, $\text{Sm}_{1-x}\text{Y}_x\text{B}_6$ and $\text{Sm}_{1-x}\text{Th}_x\text{B}_6$.

Fig. 6. — Average samarium valence determined from magnetic susceptibility measurements at 300 K in the $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ systems ($M = \text{Yb}^{2+}$, Sr^{2+} , Y^{3+} , La^{3+} , Th^{4+}).

where $\chi_{\text{Sm}^{3+}}$ and $\chi_{\text{Sm}^{2+}}$ 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 $\text{Sm}_{1-x}\text{Yb}_x\text{B}_6$ and $\text{Sm}_{1-x}\text{Sr}_x\text{B}_6$ systems; a similar remark can be made with the $\text{Sm}_{1-x}\text{La}_x\text{B}_6$ and $\text{Sm}_{1-x}\text{Y}_x\text{B}_6$ systems. Let us note that the average samarium valence with $M = \text{Th}^{4+}$ decreases more rapidly than with $M = \text{La}^{3+}$ and Y^{3+} .

The variation of the cubic lattice parameter of the $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ 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 : $r_{\text{Sm}^{2+}} > r_{\text{Sm}^{3+}}$) 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

$$(\text{Sm}_{1-y}^{2+}\text{Sm}_y^{3+})_{1-x}\text{M}_x\text{B}_6.$$

Fig. 7. — Variation of the lattice constant as a function of x in the $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ systems: a) $\text{M} = \text{Yb}^{2+}, \text{Sr}^{2+}, \text{La}^{3+}$; b) $\text{M} = \text{Y}^{3+}, \text{Th}^{4+}$.

Fig. 8. — Average samarium valence at 300 K in the $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ systems. Comparison of the results given by different methods. ● (black circles) X-ray absorption; ○ (open circles) magnetic

susceptibility; □ (open squares) lattice parameter variation. a) $\text{M} = \text{La}^{3+}$; b) $\text{M} = \text{Sr}^{2+}$; c) $\text{M} = \text{Yb}^{2+}$; d) $\text{M} = \text{Y}^{3+}$.

These compounds can be considered as solid solutions between the hypothetical hexaborides $\text{Sm}_{1-x}^{2+}\text{M}_x\text{B}_6$ and $\text{Sm}_{1-x}^{3+}\text{M}_x\text{B}_6$ 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 ($a = 4.186 \text{ \AA}$) and pure trivalent ($a = 4.115 \text{ \AA}$) 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 $\text{Eu}_{1-x}^{2+}\text{La}_x^{3+}\text{B}_6$, $\text{Eu}_{1-x}^{2+}\text{Gd}_x^{3+}\text{B}_6$ and $\text{Eu}_{1-x}^{2+}\text{Y}_x^{3+}\text{B}_6$ systems [3]. This method gives results in good agreement with those deduced from X-ray absorption and magnetic susceptibility measurements for the $\text{Sm}_{1-x}\text{Yb}_x^{2+}\text{B}_6$, $\text{Sm}_{1-x}\text{La}_x^{3+}\text{B}_6$ and $\text{Sm}_{1-x}\text{Y}_x^{3+}\text{B}_6$ systems. The method is valid only for concentrations less than $x \simeq 0.5$ in the $\text{Sm}_{1-x}\text{Sr}_x\text{B}_6$ 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 para-

meter) that the hexaborides $\text{Sm}_{1-x}\text{M}_x\text{B}_6$ ($\text{M} = \text{Yb}^{2+}$, Sr^{2+} , La^{3+} , Y^{3+} , Th^{4+}) are mixed valent compounds for $0 \leq x < 1$. The decrease of the $\text{Sm}^{2+} : \text{Sm}^{3+}$ ratio as x increases in

hexaborides suggests that the 4f levels, and therefore the Fermi level are lowered with respect to the bottom of the $5d_{eg}$ 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 ($\text{Sm}^{3+} + e^- \rightarrow \text{Sm}^{2+}$).

Acknowledgments. — The authors thank P. Lagarde and his coworkers at the Laboratoire de l'Accélérateur Linéaire (LURE), Orsay, France, for their technical assistance in the X-ray absorption measurements.

References

- [1] COHEN, R. L., EIBSCHUTZ, M. and WEST, K. W., *Phys. Rev. Lett.* **24** (1970) 383.
- [2] TARASCON, J. M., ISIKAWA, Y., CHEVALIER, B., ETOURNEAU, J., HAGENMULLER, P. and KASAYA, M., *J. Physique* **41** (1980) 1141.
- [3] MERCURIO, J. P., ETOURNEAU, J., NASLAIN, R., HAGENMULLER, P. and GOODENOUGH, J. B., *Solid State Chem.* **9** (1974) 37.
- [4] ETOURNEAU, J., MERCURIO, J. P., NASLAIN, R. and HAGENMULLER, P., *J. Solid State Chem.* **2** (1970) 332.
- [5] KASAYA, M., TARASCON, J. M. and ETOURNEAU, J., *Solid State Commun.* **33** (1980) 1005.
- [6] RAWISO, M., thèse 3^e cycle, Université Paris VI (1979).
- [7] VAINSHTEIN, E. E., BLOKHIN, S. M. and PADERNO, Yu B., *Sov. Phys. Solid State* **6** (1965) 2318.