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Temperature dependence of the samarium oxidation state in SmB_6 and $Sm_{1-x}La_xB_6$

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Résumé. — La variation thermique du paramètre de la maille cristalline de SmB_6 ainsi que des mesures d'absorption X (seuil L_{III} du samarium) effectuées entre 4,2 K et 300 K mettent en évidence une variation du degré d'oxydation moyen du samarium qui passe de 2,60 à 300 K à 2,53 à 4,2 K. Les travaux antérieurs jusqu'à présent indiquaient que le rapport Sm^{2+}/Sm^{3+} était indépendant de la température. Un comportement analogue à celui de SmB_6 a été observé pour la solution solide $Sm_{0,75}La_{0,25}B_6$.

Abstract. — The cubic lattice parameter temperature dependence of SmB_6 between 300 K and 4.2 K as well as the X-ray absorption at the L_{III} edge measured in the same temperature range, give direct evidence of the average samarium valence change which goes from 2.60 at 300 K to 2.53 at 4.2 K. Previous work claimed that the Sm^{2+} : Sm^{3+} ratio was temperature independent in SmB_6. As for SmB_6 a samarium valence change has been observed with decreasing temperature below 300 K in the $Sm_{0.75}La_{0.25}B_6$ solid solution.

Samarium hexaboride SmB_6 has attracted much experimental and theoretical attention in the last few years. SmB_6 is a homogeneous mixed valent compound in which the Sm^{2+} : Sm^{3+} ratio at room temperature has been estimated to be about 4 : 6 from magnetic susceptibility, Mössbauer resonance measurements, L_{III} X-ray absorption, and X-ray photoelectron spectroscopy (XPS) [1-10].

Furthermore previous Mössbauer resonance and X-ray absorption experiments performed respectively down to 1.1 K and 150 K had not indicated significant variations of the Sm^{2+} : Sm^{3+} ratio [3, 4, 5]. On the other hand, the lattice-parameter measurements carried out previously by us between 300 K and 4.2 K suggested a samarium valence change in SmB_6 [5, 11].

In the dynamic (homogeneous) mixed valence state, each rare earth ion can be viewed as fluctuating between two configurations with the 4f shell occupation number differing by one. The charge fluctuation time τ_F is such that *fast* measurements like X-ray absorption or XPS detect both configurations separately, while *slow* measurements such as Mössbauer isomer shift detect only an average time, in the homogeneous mixed valent compounds.

In order to determine quantitatively the samarium valence change in SmB_6 as a function of temperature, X-ray absorption measurements have been carried out. The results obtained by direct observation will be compared with those deduced from lattice parameter temperature dependence.

1. **Experimental.** — SmB_6 has been prepared according to the reaction

$$2\,Sm_2O_3 + 30\,B \rightarrow 4\,SmB_6 + 6\,B\overset{\nearrow}{O} \quad [12]\,.$$

Density measurements, X-ray and chemical analysis indicate an atomic ratio B/Sm $\simeq$ 6.

The cubic lattice parameter temperature dependence of SmB_6 and $Sm_{0.75}La_{0.25}B_6$ have been studied between 300 K and 4.2 K with a X-ray powder diffractometer using a monochromatic CoK_α X-ray radiation [13].

The X-ray absorption experiments have been performed at the French synchrotron in Orsay (LURE). The X-ray beam is emitted by 1.72 GeV electrons in the ring D.C.I. The radiation was monochromatized with the help of a (220) silicon crystal. The

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energy resolution was 2.3 eV. Intensities have been measured before and after sample through conventional ionization chambers.

2. **Results and discussion.** — 2.1 LATTICE PARAMETER TEMPERATURE DEPENDENCE. — A change in the electronic configuration of samarium, from trivalent to divalent, with decreasing temperature has been suggested by the observation that the size of the SmB_6 unit cell goes through a smooth minimum near 150 K (Fig. 1) [5, 11].

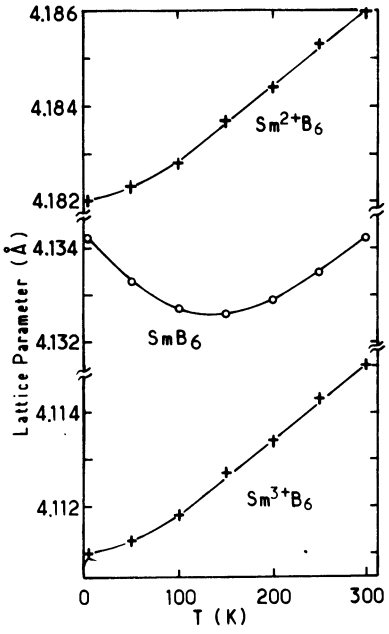


Fig. 1. — Lattice parameter temperature dependence of the cubic unit cell of SmB_6 (experimental) and of the hypothetical hexaborides $Sm^{2+}B_6$ and $Sm^{3+}B_6$ (calculated).

An estimate of the average samarium valence in SmB_6 may be deduced at any temperature from the cubic lattice parameter temperature dependence. SmB_6 can be considered as a solid solution between the hypothetical hexaborides $Sm^{2+}B_6$ and $Sm^{3+}B_6$ for which the lattice parameters have been interpolated from those of neighbouring divalent and trivalent rare earth hexaborides. We can deduce the thermal expansion of the unit cell of « $Sm^{2+}B_6$ » and « $Sm^{3+}B_6$ » below 300 K from those of the other hexaborides (YbB_6, SrB_6, LaB_6) for which the thermal variation of the lattice parameter is approximately the same.

It is worthwhile to note that in the systems $M^{2+}_{1-x}M^{3+}_{x}B_6$ the variation of the cubic lattice parameter does not follow a Vegard rule. For instance, the variation of the lattice parameter in the $Eu^{2+}_{1-x}La^{3+}_{x}B_6$, $Eu^{2+}_{1-x}Gd^{3+}_{x}B_6$ and $Yb^{2+}_{1-x}Gd^{3+}_{x}B_6$ system shows a concave curve. This deviation from a Vegard rule is due to the presence of electrons in the $5de_g$ conduction band [14, 15]. These results have been used to estimate the deviation in a theoretical $Sm^{2+}_{1-x}Sm^{3+}_{x}B_6$ solid solution. The variation of the lattice parameter of $Sm^{2+}_{1-x}Sm^{3+}_{x}B_6$ as a function of x is given in figure 2 at 300 K.

With such an approach, the experimental value of the SmB_6 lattice parameter at 300 K

$$(a = 4.134\,2 \pm 5 \times 10^{-4}\ \text{Å})$$

corresponds to $x \simeq 0.6$, that is, 2.60 for the average samarium valence in SmB_6. This result agrees well with those obtained by magnetic measurements and XPS studies [7, 8].

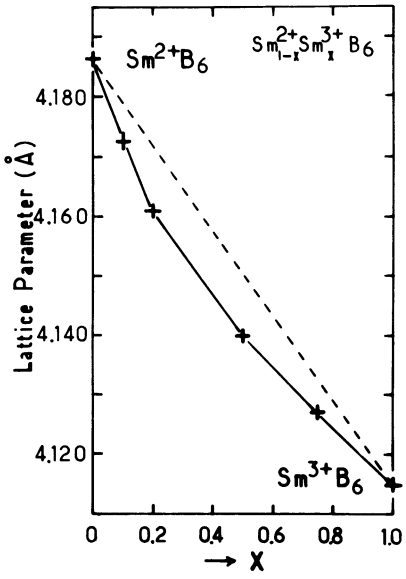


Fig. 2. — Calculated variation of the cubic lattice parameter as a function of x at 300 K for the $Sm^{2+}_{1-x}Sm^{3+}_{x}B_6$ system.

The variation of the lattice parameter of $Sm^{2+}_{1-x}Sm^{3+}_{x}B_6$ as a function of x, calculated at any temperature between 300 K and 4.2 K, and the temperature dependence of the lattice parameter of SmB_6, allowed us to propose the variation of the average samarium valence as a function of temperature (Fig. 3).

As the temperature decreases from 300 K down to 4.2 K the average samarium valence change in SmB_6 goes from 2.60 to 2.53, corresponding to an increase of 17.5 % of Sm^{2+} ions.

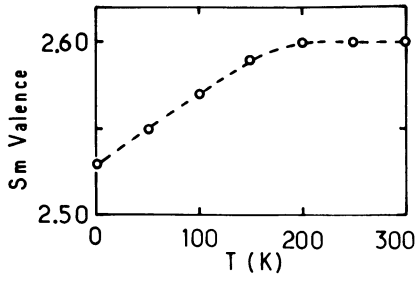


Fig. 3. — Average samarium valence temperature dependence in SmB_6 between 300 K and 4.2 K.

2.2 X-RAY ABSORPTION. — X-ray absorption at the L_{III} edge has been measured from 300 K to 4.2 K in SmB_6. The structure of the absorption spectrum within a few eV of an edge allows to extract the fractional valence of the bulk to within a few % [3].

The L_{III} absorption spectra obtained consist of two peaks corresponding to the spectral components of Sm^{2+} and Sm^{3+} valence states separated by 7 eV (Figs. 4 and 5).

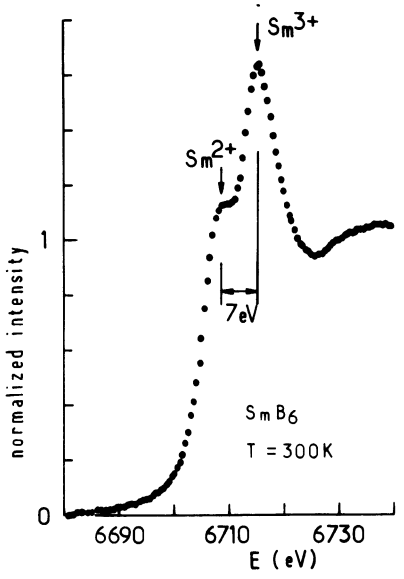


Fig. 4. — Structure of the SmL_{III} absorption edge in SmB_6 at 300 K (sample outside the cryostat).

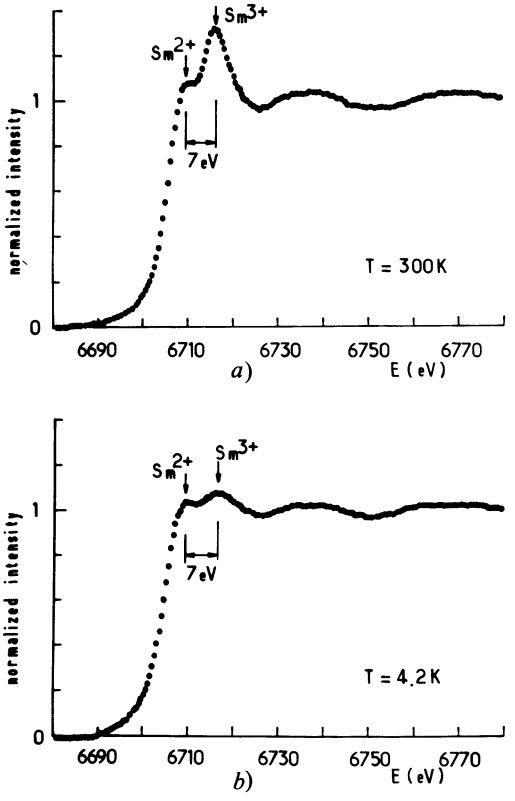


Fig. 5. — Structure of the SmL_{III} absorption edge in SmB_6 (sample inside the cryostat). *a*) at 300 K ; *b*) at 4.2 K.

The difference in intensities of the Sm^{2+} and Sm^{3+} lines between the spectra given in figures 4 and 5*a* comes from changes in sample thickness and homogeneity. The intensity of the Sm^{3+} peak, with respect to that of Sm^{2+} peak, decreases as the temperature decreases. The difference between the absorption curve before the edge and the mean absorption averaged over the EXAFS oscillations after the edge is normalized to one.

The absorption curves have been plotted considering the fact that the shape of the L_{III} absorption edge remains unchanged whatever the oxidation state (+ II or + III) of a given rare earth cation in the hexaborides [3]. Then, the L_{III} absorption spectrum of Eu^{2+} in EuB_6 has been chosen as reference and the analysis of the experimental absorption curves has been made by fractional superposition of two EuB_6L_{III} absorption spectra shifted with respect to each other by 7 eV (Fig. 6).

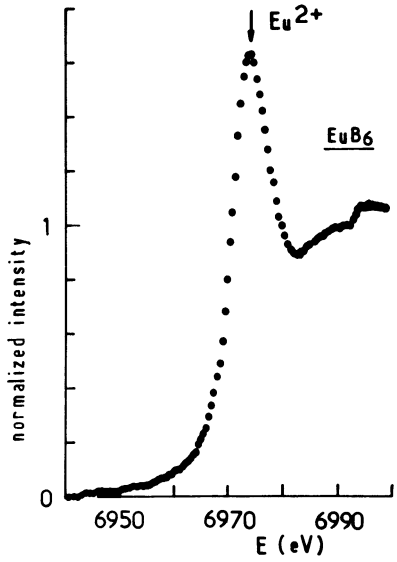
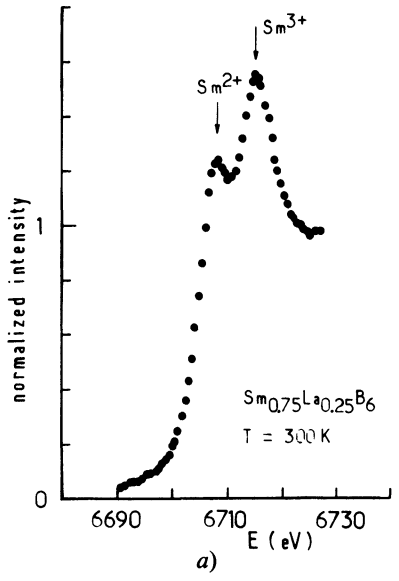


Fig. 6. — Structure of the $Eu^{2+}L_{III}$ absorption edge in EuB_6 at 300 K.

The plotting of the experimental L_{III} absorption curves of SmB_6 indicates a temperature dependence of the average samarium valence in good agreement with the results deduced from the lattice parameter temperature dependence. At room temperature, the average samarium valence is found to be 2.58 ± 0.02 and decreases about 3 % as the temperature reaches 4.2 K.

As for SmB_6 itself, the average samarium valence is temperature dependent in the $Sm_{1-x}La_xB_6$ system. The X-ray absorption measurements at the L_{III} edge carried out at 300 K and at 4.2 K for $x = 0.25$ indicate an increase of the Sm^{2+} : Sm^{3+} ratio with decreasing temperature (Fig. 7). This observation is confirmed by the variation of the lattice parameter as a function of temperature, which goes through a minimum at about 200 K (Fig. 8). The average samarium valence deduced from the plotting of the



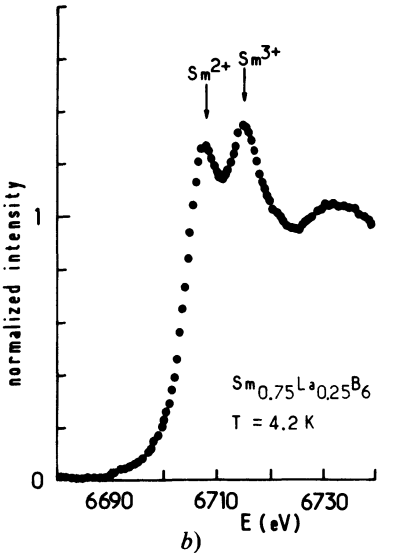


Fig. 7. — Structure of the SmL_{III} absorption edge in the $Sm_{0.75}La_{0.25}B_6$ solid solution. *a*) at 300 K ; *b*) at 4.2 K (sample inside the cryostat).

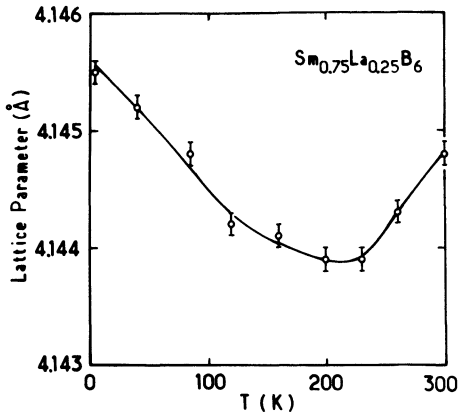


Fig. 8. — Lattice temperature dependence of the $Sm_{0.75}La_{0.25}B_6$ solid solution between 300 K and 4.2 K.

X-ray absorption spectra is in good agreement with those deduced from the lattice parameter temperature dependence : 2.44 at 300 K and 2.35 at 4.2 K.

For the first time, direct evidence for a change of the electronic configuration of samarium from trivalent to divalent with decreasing temperature has been found in SmB_6 and $Sm_{0.75}La_{0.25}B_6$. These compounds are considered as homogeneous mixed valent compounds : in other words, with 4f and $5de_g$ conduction band states present at the Fermi level [16].

In the case of SmB_6, the $5de_g$ conduction band is occupied by about 0.6 conduction electron per Sm atom at 300 K. Due to the higher electronic localization of the $4f^6$ level ($Sm^{3+} + e^- \rightarrow Sm^{2+}$) the number of free carriers decreases, involving an increase of the resistivity at low temperature. However, this effect is too small to explain the strong increase of the resistivity observed below 100 K. So far, the resistivity temperature dependence below 100 K is explained by the presence of an energy gap near the Fermi level due to either f-d hybridization or the formation of a Wigner lattice [17, 18].

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