Vol. **126** (2014) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Investigation of Mixed Valence State of $Sm_{1-x}B_6$ and $Sm_{1-x}La_xB_6$ by XANES

S. Gabáni[a,*], K. Flachbart[a], J. Bednarčík[b], E. Welter[b], V. Filipov[c], N. Shitsevalova[c]
[a]Centre of Low Temp. Physics, Institute of Experimental Physics SAS, Watsonova 47, 04001 Košice, Slovakia
[b]Deutsches Elektronen Synchrotron DESY, Notkestrasse 85, 22603 Hamburg, Germany
[c]Institute for Problems of Materials Science, NASU, Krzhyzhanovsky 3, 03680 Kiev, Ukraine

We investigated the valence states of samarium ions in Sm deficient $Sm_{1-x}B_6$ ($x = 0.03$, 0.05, 0.08, 0.1 and 0.2) sintered samples, in single crystalline solid solutions $Sm_{1-x}La_xB_6$ ($x = 0.16$, 0.28, 0.4, 0.55 and 0.7) as well as in a SmB_6 single crystal by X-ray absorption near edge structure (XANES) between 4.2 and 300 K. It was shown that the mixed valence state v_{Sm} of Sm-ions ($v_{Sm} \approx 2.51$ for SmB_6 at 4.2 K) in deficient samples is changed but maintained up to a concentration of 20% of vacancies and up to a concentration of 70% in samples doped with trivalent La-ions, and that in both cases it increases with temperature. On the other hand, the value of v_{Sm} increases with increasing vacancy level, whereas it decreases with increasing La^{3+} substitution. The obtained dependences of Sm-valence in SmB_6 on vacancy as well as on La^{3+} ion concentration are in good agreement with susceptibility measurements and exact numerical calculation of the spinless Falicov-Kimball model in two dimensions.

DOI: 10.12693/APhysPolA.126.338

PACS: 78.70.Dm, 71.28.+d, 71.27.+a

1. Introduction

SmB_6 is the prototype of intermediate valence (IV) compounds and is one of the most studied materials of this class [1]. The Sm ions on equivalent sites in SmB_6 can be considered to be in $4f^6$(Sm^{2+}) or $4f^5 5d^1$(Sm^{3+}) configurations. The ratio $4f^6$:$4f^5 5d^1$ is about 4:6 (Sm valence $v \propto 2.6$) and changes weakly with temperature: $v(300\text{ K}) = 2.59 - 2.66$ and $v(4.2\text{ K}) = 2.52$ [2, 3]. Much more significant is the influence of doping on valence states in this compound. The substitution of Sm by nonmagnetic divalent ions (e. g. Sr^{2+}, Yb^{2+}) increases the average samarium valence, whereas the substitution of Sm by nonmagnetic trivalent ions (e. g. Y^{3+}, La^{3+}) produces the opposite effect [2, 4]. Recently Raman scattering study of rare-earth hexaborides has shown that at room temperature the Sm valence increases with increasing applied pressure, and all Sm ions become trivalent at about 20 GPa in SmB_6 [5].

The usual explanation [1 – 3] of the Sm-valence dependence on concentration of defects and impurities is the shift of the $4f$ level with respect to the Fermi level or the bottom of conduction band. It has been found that the spinless Falicov-Kimball model (FKM) can describe the discontinuous valence and insulator-metal transition in SmB_6, as well as the behavior of the average samarium valence in $Sm_{1-x}M_xB_6$ systems (M=Y^{3+}, La^{3+}, Sr^{2+}, Yb^{2+}), in a very good qualitative and quantitative agreement with experimental results [6]. In case of $Sm_{1-x}B_6$ the stabilization of the boron sublattice and the effect of chemical pressure have also to be taken into account.

The aim of the present work is to observe the influence of doping by La^{3+} ions and especially the "doping" by vacancies in SmB_6 on the X-ray absorption spectra, and hence on the ground state properties of this compound, as such investigations are very rare [7].

2. Experimental details

Completely new sintered samples of $Sm_{1-x}B_6$ ($x = 0.03$, 0.05, 0.08, 0.1 and 0.2) have been prepared from powdered samples which were synthesized and analyzed according to a method described previously [7]. However, two additional firing processes have to be made to receive the one-phase-homogeneous crystal structure. As a result the continuous change of the lattice parameter was found, as a function of the amount of vacancies [7]. High-quality single crystals of SmB_6 and $Sm_{1-x}La_xB_6$ solid solutions with $x = 0.16$, 0.28, 0.4, 0.55 and 0.7 were grown by vertical crucible-free induction zone melting in an inert gas atmosphere. The X-ray absorption near edge structure (XANES) measurements between 4.2 and 300 K were carried out at the bending beamline A1 of the DORIS III positron storage ring at DESY using a ^{4}He Optistat CF DY cryostat from Oxford Instruments.

3. Results and discussion

In case of SmB_6, the XANES region of Sm-L_{III} absorption edge reveals two distinct resonances which reflect the mixed valence state in this compound. In order to describe such a state quantitatively, we performed fitting of XANES spectra. The data analysis of spectra started with pre-edge background removal, which was modeled assuming a linear dependence. Spectra were further normalized in the way that the absorption step was always equal to one. According to [8], the XANES region can be deconvoluted into threshold resonance line components and an underlying "step", representing the onset of absorption to continuum states. In our case we assumed

---

*corresponding author; e-mail: gabani@saske.sk

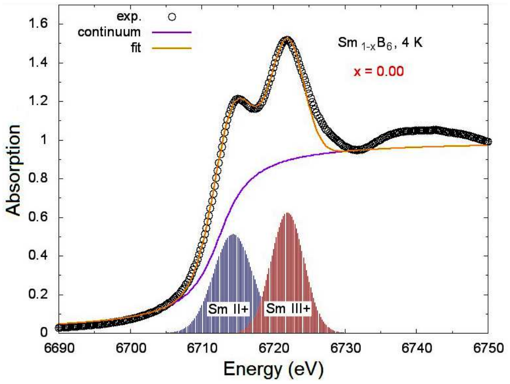

Fig. 1. Fitted XANES spectra of SmB_6 at 4.2 K with deconvoluted contributions.

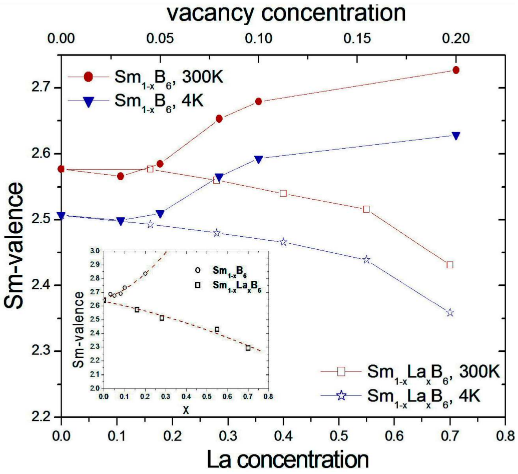

Fig. 2. Phase diagram of Sm-valence vs. vacancy or La^{3+} ions concentration, respectively. In inset results obtained from analysis of susceptibility [4] are shown.

two Gaussian profiles for two resonance lines, the continuum was modeled using an inverse tangent function. The XANES region was described by following function:

$$F(x) = \left[\frac{1}{2} + \frac{1}{\pi}\arctan\left(\gamma\left(x - E_0\right)\right)\right] + \sum_{i=2}^{3} A_i \exp\left(-\log 2\left(\frac{x - E_i}{w_i}\right)^2\right), \qquad (1)$$

where E_0 and γ are the absorption edge and steepness of continuum, respectively, A_i, E_i and $2w_i$ denote amplitude, position and full-width at half-maximum of corresponding resonance lines ($i = 2, 3$), respectively. XANES spectra in energy range between 6710 and 6725 eV were fitted by Eq. 1 using a non-linear least square method. Parameters describing the continuum, E_0 ($= 6712.5$ eV) and γ ($= 0.3$) were fixed, whereas the resonance line profile parameters A_i, E_i and w_i ($i = 2, 3$) were refined. The resulting valence "v" is proportional to relative areas of resonance lines and can be defined as [9]:

$$v = 2 + \frac{A_3 w_3}{A_2 w_2 + A_3 w_3}. \qquad (2)$$

An example of fitted XANES spectra of SmB_6 measured at 4.2 K is shown in Fig. 1. Good agreement between the proposed model (Eq. 1) and measured data was observed. Similar fits were performed at different temperatures for both series of samples, $Sm_{1-x}B_6$ and $Sm_{1-x}La_xB_6$. The resulting variation of the Sm-ion valence as a function of concentration of vacancies and La^{3+} ions (Fig. 2) shows that the IV state of Sm ions is maintained in $Sm_{1-x}B_6$ samples up to 20 % of concentration x of vacancies and the valence increases with increasing x. These results are in good qualitative agreement with susceptibility and X-ray measurements [4, 7] and exact numerical calculation of the spinless FKM in two dimensions [10]. This theoretical study of $Sm_{1-x}B_6$ has shown that the valence transition of Sm ions is maintained up to 25% of vacancy concentration x and that the average f-orbital occupancy, $n_f = 3 - v$, decreases with x. It means that Sm valence behaves in the same way for vacancies as for divalent impurities [2, 6].

Thus, based on XANES measurements, we conclude that the mixed valence state of Sm-ions in SmB_6 samples containing vacancies is maintained up to 20% of their concentration and increases with increasing vacancy level, similarly as in SmB_6 samples doped by divalent ions.

Acknowledgments

This work was supported by DESY project I-20100068 EC, by projects VEGA 2/0106/13, APVV 0132-11, and by CFNT MVEP project of the Slovak Academy of Sciences.

References

[1] P.S. Riseborough, *Adv. Phys.* **49**, 257 (2000).
[2] J.M. Tarascon, Y. Isikawa, B. Chevalier, J. Etourneau, P. Hagenmuller, M. Kasaya, *J. de Phys.* **41**, 1135 (1980); *ibid.*, p. 1141.
[3] M. Mizumaki, S. Tsutsui, F. Iga, *J. Phys.: Conf. Series* **176**, 012034 (2009).
[4] S. Gabani, K. Flachbart, V. Pavlík, T. Herrmannsdörfer, E. Konovalova, Y. Paderno, J. Briančin, J. Trpčevská, *Czech. J. Phys.* **52**, A225 (2002).
[5] N. Ogita, S. Nagai, M. Udagawa, F. Iga, M. Sera, T. Oguchi, J. Akimitsu, S. Kunii, *Physica B* **359-361**, 941 (2005).
[6] P. Farkasovksy, *Solid State Commun.* **135**, 273 (2005).
[7] N. Shitsevalova, *Ph.D. Thesis* University of Wroclaw, Poland 2001.
[8] J.A. Hoersley, *J. Chem. Phys.* **76**, 1451 (1982).
[9] M. Mizumaki, S. Tsutsui, H. Tanida, T. Uruga, D. Kikuchi, H. Sugawara, H. Sato, *J. Phys. Soc. Jpn.* **76**, 053706 (2007).
[10] M. Zonda, P. Farkasovsky, H. Cencarikova, *Acta Physica Polonica* **113**, 291 (2008).