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Local crystalline structure of Sm-Co alloys: results of XAFS-analysis

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Abstract. Local crystalline structure of hypo- and hyperstoichiometric SmCoₓ alloys with 𝑥 = 5.15, 4.95, 4.0, 3.75 heat treated in different conditions was investigated by means of the X-ray absorption spectroscopy. Experimental spectra were measured above the L₃-Sm absorption edge. EXAFS-analysis shows that stacking faults appear in hyperstoichiometric alloys SmCo₄ and SmCo₃.₇₅, confirming the hypothesis of “high coercive state, induced by phase transformations, changing the state of the grain surface in basic phase”. L₃-Sm XANES spectra demonstrate the reduction of the “white line” amplitude in Sm-enriched samples.

1. Introduction
Synthesis of the SmCo₅ compound has become the new advanced stage in development of hard magnetic materials [1]. The highest coercive force (Hci) was received for Sm-enriched (SmCo₅₋ₙ) magnets prepared by sintering. Post sintering heat treatment (HT) is an important stage of magnets processing. Conventional HT includes slow cooling from 1120 to 850°C and rapid cooling to room temperature [2]. Such HT increases Hci of sintered magnets from 0.1 to more than 3.5 T. To explain this phenomenon there was proposed the “perfect lattice” hypothesis [3], but it appears to contradict several experimental facts. So the new mechanism of phase transformation-induced coercivity in sintered SmCo₅₋ₙ magnets was developed based on X-ray diffraction (XRD) data in [4, 5]. According to these data the changes of lattice parameters of SmCo₅ phase after ageing at 1200-800°C correspond to the growth of Sm content in SmCo₅ at lower ageing temperature [6, 7]. Details of Sm enrichment process on atomic level are yet under discussion. Probably it is concerned with disordered stacking defects formation [8]. These defects cannot be revealed by XRD methods as they do not produce supercell reflexes, so we have investigated the local atomic structure of SmCo₅₋ₙ alloys using the X-ray absorption fine structure (XAFS) technique.

2. Experimental
Ingots with nominal composition of SmCoₓ (𝑥 = 5.15 (sample N1), 4.95 (N2), 4.0 (N3), 3.75 (N4)) were prepared by induction melting in Ar atmosphere followed by casting in an iron mould. The samples were then aged in a vacuum furnace in series: 1220°C for 3 h + 1000°C for 5 h +
900°C for 10 h. After each step of ageing the samples were cooled inside the furnace to room temperature. Phase identification was carried out by XRD using CuKα radiation.

X-ray absorption spectra were collected at E4 beamline of the DORIS III (DESY, Hamburg, Germany) synchrotron, at the $L_3$ edge of Sm (6716 eV). Energy resolution of the double-crystal Si (111) monochromator with a 0.3 mm slit was about 0.9 eV at 7 keV. Low-temperature measurements were carried out using a liquid-helium flow cryostat, temperature instability didn’t exceed ±1 K at 300 K and 0.1 K at 4 K.

EXAFS spectra analysis was performed using the VIPER [9] software pack. The background in the experimental spectra was removed as described in [10], taking care to remove the low-frequency oscillations. The EXAFS functions $\chi(k)k^2$ obtained from the absorption spectra above Sm $L_3$ edge were Fourier transformed (FT) in the range of wavenumber $k$ from 2 to 12 Å$^{-1}$, using the Kaiser-Bessel windowing function. Fourier back-transformation (BFT) was carried out using a Hanning window from $\sim$1.9 to $\sim$3.6 Å corresponding to the closest near-neighbouring shells. BFT modelling was performed according to formula:

$$\chi(k) = -S_0^2 \sum_j N_j \frac{|f_j(\pi, k)|}{kR_j^2} \sin(2kR_j + \phi_j(k)) \exp(-2\sigma_j^2k^2)$$  \hspace{1cm} (1)

where $R_j$ — mean radius of $j$-th sphere, $\sigma_j^2$ — Debye-Waller factor (mean-square deviation of interatomic distance), $S_0^2$ — many-body reduction factor, $f_j(\pi, k)$ and $\phi_j(k)$ — back-scattering amplitude and phase shift calculated by FEFF [11].

3. Results

Near edge structure of Sm absorption spectra (fig. 1) contains information on electronic properties of Sm ions. Area below the “white line” of $L_3$-absorption denotes the quantity of unoccupied states in a 5$d$-band, so small reduction of the white line amplitude on Sm enrichment means that the filling of Sm 5$d$-band raises. We can suppose that excess Sm ions have a valence of 3+ because divalent samarium ions do not contribute the 5$d$-band.

![Figure 1](image1.png)

Figure 1. $L_3$-Sm XANES at 4.2 K for SmCo$_x$ alloys after ageing at 900°C.

![Figure 2](image2.png)

Figure 2. $L_3$-Sm EXAFS BFT at 4.2 K for SmCo$_x$ alloys after ageing at 900°C.

$L_3$-Sm EXAFS back Fourier transformations for SmCo$_x$ samples are shown on fig. 2. One can notice significant difference in the shape of the spectra for samples N1–N2 having stoichiometry
close to SmCo$_5$ compared to samples N3-N4 consisting of SmCo$_5$ and Sm$_2$Co$_7$ phases. Under ageing at 900$^\circ$C a small amount of Sm$_2$Co$_{17}$ phase is formed in hypostoichiometric alloy N1 due to decomposition of SmCo$_{5+y}$ solid solution.

Diphasic samples (N3-N4) are characterized by significant restructuring of samarium local environment in comparison with monophase (N2). Modelling shows that two nearest spheres of samarium local environment in all samples are formed by Co atoms only. Two-sphere model 6Co-12Co provides satisfactory quality of fitting for monophase samples (fig. 3) whereas we had to use 3-sphere 6Co-(12-x)Co-xSm model for diphasic alloys (fig. 4). This once again confirms Co atoms substitution with samarium in SmCo$_5$ lattice of Sm-enriched alloys (N3-N4) after heat treatment at low temperature.

This fact points out that stoichiometric (N2) and hypostoichiometric (N1) samples consist of practically pure SmCo$_5$ phase but this phase is locally transformed in hyperstoichiometric ones. The initial structure of hexagonal SmCo$_5$ phase (type D$_2$d), shown on fig. 5, can be described as a sequence of (Abc)$\alpha$ blocks stacked without any shift in the (001) plane. The mixed Sm-Co layer (Abc) consists of 3 nets: A composed of Sm-atoms, b and c constituted by Co-atoms. The b and c nets are displaced with regard to A-net by $t = 1/3a\langle 110 \rangle$ and $-t$, respectively. The $\alpha$-layer consists of Co-atoms only. The initial block (Abc)$\alpha$ shifted by vectors $t$ and $-t$ turns into (Bca)$\beta$ and (Cab)$\gamma$ correspondingly. Formation of stacking faults is accompanied by displacement of (Abc)-layer by vector $t$, removal of the $\alpha$-layer in the stacking fault plane and shift of Sm-layers $A$ and $B$ towards each other to a short distance along $\langle 001 \rangle$ directions (fig. 6). Sm-layers $A$ and $B$ approach results in reduction of the lattice parameter $c$ of the average block thickness. Moreover, neighboring Sm atoms in layers $A$ and $B$ are too close to each other, therefore extension of lattice in the basic plane, i.e. lattice parameter $a$ increase, is needed. Thus insertion of randomly distributed stacking faults in SmCo$_5$ phase due to Sm enrichment, results in increase of $a$ and decrease of $c$ lattice parameters. So we suppose that disordered stacking faults are formed in Sm enriched alloys and this fact is confirmed by XRD experiments revealing changes in lattice parameters of SmCo$_5$ phase characteristic of this phenomenon and by value of interatomic Sm-Sm distance in 3-sphere model.
4. Conclusions

Noticeable difference in EXAFS-function of the investigated SmCoₓ alloys is an evidence of significant changes in samarium local environment upon enrichment of the stoichiometric SmCo₅ compound with excessive samarium atoms. Observed effects may be a consequence of the transformation to the Sm enriched phase SmCo₅₋ₓ accompanied by creation of disordered stacking faults: shift by a Burgers vector \( \mathbf{t} = \frac{1}{3}a\langle 110 \rangle \) and removal of the interstitial Co layer. Obtained results agree with the XRD data and confirm the hypothesis of “high coercive state, induced by phase transformations, changing the state of the grain surface in basic phase” [5]. Examination of the near edge structure of L₃-Sm absorption revealed that enrichment of the parent phase with samarium leads to the raise of Sm 5d - band filling.

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