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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 SmCo_x 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 L_3-Sm absorption edge. EXAFS-analysis shows that stacking faults appear in hyperstoichiometric alloys SmCo_4 and $\mathrm{SmCo}_{3.75}$, confirming the hypothesis of "high coercive state, induced by phase transformations, changing the state of the grain surface in basic phase". L_3-Sm XANES spectra demonstrate the reduction of the "white line" amplitude in Sm-enriched samples.

1. Introduction

Synthesis of the SmCo_5 compound has become the new advanced stage in development of hard magnetic materials [1]. The highest coercive force (H_{ci}) was received for Sm-enriched (SmCo_{5-y}) 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 H_{ci} 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 SmCo_{5-y} magnets was developed based on X-ray diffraction (XRD) data in [4, 5]. According to these data the changes of lattice parameters of SmCo_5 phase after ageing at 1200-800°C correspond to the growth of Sm content in SmCo_5 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 SmCo_{5-y} alloys using the X-ray absorption fine structure (XAFS) technique.

2. Experimental

Ingots with nominal composition of SmCo_x ($x = 5.15$ (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 CuK_α 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 didnt 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 ~1.9 to ~3.6 Å corresponding to the closest near-neighbouring shells. BFT modelling was perfomed according to formula:

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

where R_j — mean radius of j-th sphere, σ_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 5d-band, so small reduction of the white line amplitude on Sm enrichment means that the filling of Sm 5d-band raises. We can suppose that excess Sm ions have a valence of 3+ because divalent samarium ions do not contribute the 5d-band.

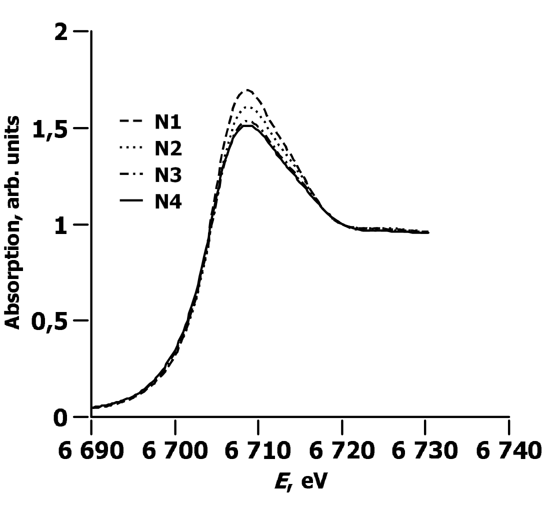

Figure 1. L_3-Sm XANES at 4.2 K for SmCo$_x$ alloys after ageing at 900°C.

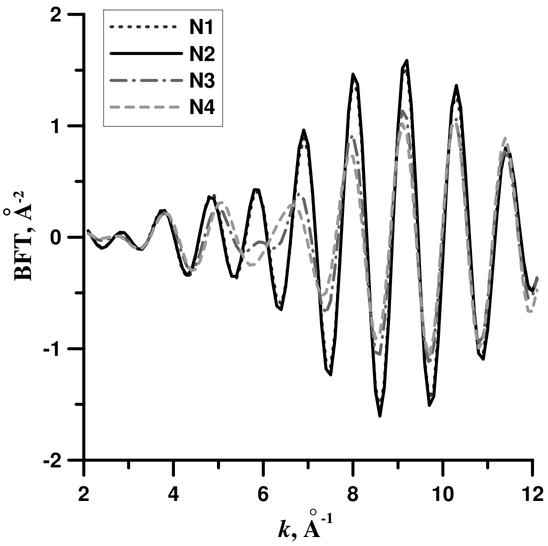

Figure 2. L_3-Sm EXAFS BFT at 4.2 K for SmCo$_x$ alloys after ageing at 900°C.

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_2Co_7 phases. Under ageing at 900°C a small amount of Sm_2Co_{17} phase is formed in hypostoichiometric alloy N1 due to decomposition of $SmCo_{5+y}$ solid solution.

Diphase 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 diphase 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.

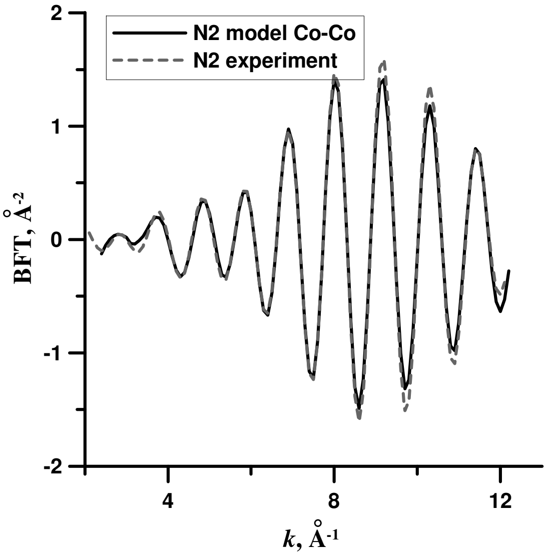

Figure 3. BFT of experimental EXAFS function at 4.2 K and model function for $SmCo_{4.95}$ alloy after ageing at 900°C.

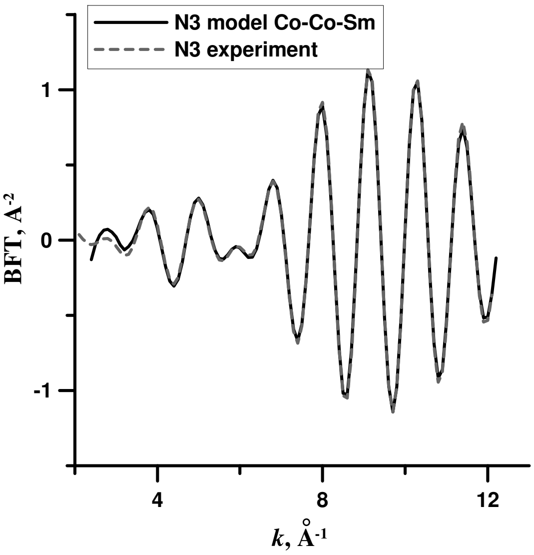

Figure 4. BFT of experimental EXAFS function at 4.2 K and model function for $SmCo_4$ alloy after ageing at 900°C.

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 $D2_d$), 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 $\mathbf{t} = 1/3a\langle 110\rangle$ and $-\mathbf{t}$, respectively. The α-layer consists of Co-atoms only. The initial block $(Abc)\alpha$ shifted by vectors $\mathbf{t}$ and $-\mathbf{t}$ turns into $(Bca)\beta$ and $(Cab)\gamma$ correspondingly. Formation of stacking faults is accompanied by displacement of (Abc)-layer by vector $\mathbf{t}$, removal of the α-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 approachment 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.

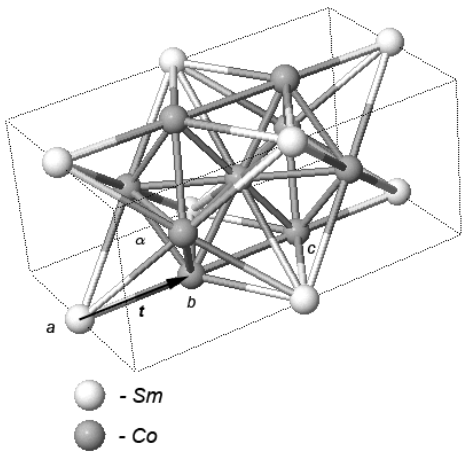

Figure 5. Crystalline structure of $SmCo_5$ alloy.

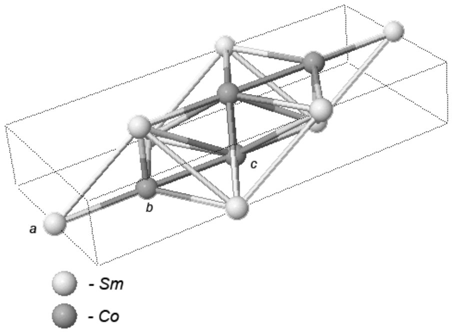

Figure 6. Crystalline structure of stacking faults in $SmCo_5$ alloy.

4. Conclusions

Noticeable difference in EXAFS-function of the investigated $SmCo_x$ alloys is an evidence of significant changes in samarium local environment upon enrichment of the stoichiometric $SmCo_5$ compound with excessive samarium atoms. Observed effects may be a consequence of the transformation to the Sm enriched phase $SmCo_{5-x}$ accompanied by creation of disordered stacking faults: shift by a Burgers vector $\mathbf{t} = 1/3a\langle 110\rangle$ 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 L_3-Sm absorption revealed that enrichment of the parent phase with samarium leads to the raise of Sm 5d - band filling.

Acknowledgments

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