Mössbauer-spectroscopic Characterization of the Local Surrounding of Tin Dopant Cations in the Bulk and on the Surface of $YCrO_3$ Crystallites

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^{119}Sn Mössbauer spectra of tin-doped $YCrO_3$, obtained by annealing in air of an $YCr(^{119}Sn^{4+})_{0.003}(OH)_6 \cdot xH_2O$ precursor, provide evidence for the location of Sn^{4+} on the Cr^{3+} site in the bulk of crystallites. Below the Néel point of $YCrO_3$ (T_N = 141 K), Sn^{4+} ions are spin-polarized, the majority exhibiting a hyperfine field H of 80 kOe at 4.2 K. Analysis of the ^{119}Sn spectra of another sample, obtained by impregnation of polycrystalline $YCrO_3$ with a solution of $^{119}SnCl_4$, shows that annealing in H_2 results in the location of the dopant, in the divalent state, on the surface of the crystallites. The parameters of an *in situ* ^{119}Sn spectrum at 295 K (isomer shift δ = 2.76 mm s^{-1} and quadrupole splitting E_Q = 1.95 mm s^{-1}) reveal the presence of Sn^{2+} ions on sites with a coordination number CN < 6. At 100 K these Sn^{2+} ions exhibit no spin polarization. Upon contact with air they are rapidly oxidized to the tetravalent state, as demonstrated by their modified isomer shift value δ = 0.06 mm s^{-1}. For the large majority of both the residual "parent" Sn^{2+} ions and the "daughter" Sn^{4+} ones no spin polarization is observed down to 4.2 K. This means that surface-located tin dopant cations, regardless of their oxidation state, occupy the Y^{3+} sites with an equal number of Cr^{3+} neighbors having mutually opposite spin orientations.

Key words: $YCrO_3$, ^{119}Sn Mössbauer Spectroscopy, Bulk and Surface Sites

Introduction

The first Mössbauer spectroscopic investigations of the hyperfine interactions of the $^{119}Sn^{4+}$ dopant in $RCrO_3$ (R = La, Y, Lu) antiferromagnetic orthochromites [1, 2] aimed to elucidate the mechanism of spin polarization of the diamagnetic tin cations by their magnetically active Cr^{3+} neighbors in perovskite-related structures. Recently, one of these orthochromites, $LuCrO_3$, was investigated in order to determine the location of the ^{119}Sn probe on surface sites of crystallites [3]. Some $RCrO_3$ compounds are actually utilized both as materials for semiconductor gas sensors and as catalysts in certain practically relevant processes, *e. g.* the oxidation of CO or C_3H_6 by O_2 [4]. The location of ^{119}Sn on the solid-gas interface would allow one to characterize, using the Mössbauer effect, the impact of tin additives on surface-sensitive properties of such materials. These experiments [3] have demonstrated that it is possible to stabilize the ^{119}Sn probes on the surface of $LuCrO_3$. However, it remained unclear whether the synthesis procedure developed in this study [3] may also be used to locate tin cations on the surface of other $RCrO_3$ substrates. In this paper, we report new results concerning ^{119}Sn dopant ions in $YCrO_3$. This chromite was chosen for the following reasons: (i) the value of the magnetic field H at the Sn^{4+} cations on the Cr^{3+} site in the bulk of crystallites is known (at 10 K, H = 75 kOe [2]). This fact facilitates the analysis of the spectra obtained for several sites of tin; (ii) the Néel point of $YCrO_3$ (T_N = 141 K [5]) is higher than that of $LuCrO_3$ (111 K [6]) investigated previously as a matrix for $^{119}Sn^{4+}$. The higher value of T_N is an advantage in studying the samples which need *in situ* low-temperature measurements which cannot be carried out at 4.2 K. For instance, in the case of $YCrO_3$, a conclusion about the occurrence or non-occurrence of the spin polarization of Sn^{2+}

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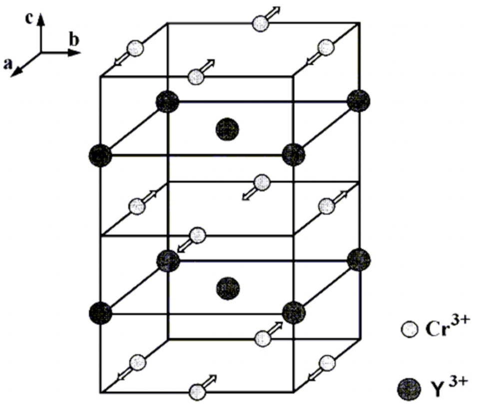

Fig. 1. Orthorhombic unit cell of $YCrO_3$. Only the Cr^{3+} and Y^{3+} sites are shown. The arrows indicate the directions of Cr^{3+} spin moments [5].

can already be drawn from the *in situ* ^{119}Sn spectrum taken at 100 K; (iii) as the saturation value of H for Sn^{4+} in $YCrO_3$ ($H_{T\rightarrow 0K}$ = 75 kOe [2]) is considerably higher than that for $LaCrO_3$ ($H_{T\rightarrow 0K}$ = 35 kOe [2]), the former chromite appears to be preferable as a magnetic substrate, despite the much higher T_N of $LaCrO_3$ (282 K [5]); (iv) the electronic shell of Y^{3+}, like that of both Lu^{3+} and La^{3+}, has no unpaired electrons. Hence, for the interpretation of magnetically split ^{119}Sn spectra, only the interactions of the dopant with neighboring Cr^{3+} cations are to be considered for $YCrO_3$ (Fig. 1).

Experimental Section

To achieve better homogeneity of the dopant distribution in the sample, the procedure of synthesis involved a coprecipitation stage. To obtain an $YCr(OH)_6{\cdot}xH_2O$ precursor, doped with 0.3 at.-% Sn, 9 mL of 10 % aqueous ammonia solution was added to 40 mL of a hot acidified aqueous solution containing chromium (III) acetate (5.4 mmol), yttrium nitrate (5.4 mmol) and stannic chloride (1.62×10^{-2} mmol) enriched to 92 % with the isotope ^{119}Sn. The precursor was filtered, washed with distilled water and dried in air at 130 °C.

An $YCrO_3$ sample containing the ^{119}Sn probe in the bulk of crystallites (sample **1**) was prepared by calcining the precursor in air at 900 °C for 26 h. To obtain an $YCrO_3$ sample with ^{119}Sn cations located on the surface sites (sample **2**), an acidified $^{119}SnCl_4$ solution was dropped on a dopant-free $YCrO_3$ powder substrate prepared under similar conditions. Prior to this treatment, $YCrO_3$ was moistened with a 10 % aqueous ammonia solution to promote fast hydrolysis of $SnCl_4$ upon contact with $YCrO_3$. The overall composition of the samples **1** and **2** was the same (molar ratio [Y]:[Cr]:[Sn] = 1:1:0.003). After being washed with water and dried in air at 130 °C, the tin-impregnated powder was calcined in H_2, first in a quartz tube at 600 °C for 1 h and then, after being transferred to a quartz reactor, at 900 °C for 2 h. Using this reactor, which was equipped with a lateral thin quartz sample cell [7], a ^{119}Sn spectrum could be taken after cooling the sample *in situ* in hydrogen atmosphere, *i. e.* out of contact with ambient air (the measurements are denoted hereafter as *in situ* Mössbauer spectroscopic measurements).

In all cases, XRD analysis of the resulting material revealed the presence of a single phase, an orthorhombically distorted $YCrO_3$ perovskite (space group *Pnma* [8, 9]).

^{119}Sn spectra were recorded using a conventional spectrometer operating in constant acceleration mode with a $Ca^{119m}SnO_3$ source (all the isomer shift values δ refer to the $BaSnO_3$ absorber at 295 K). Spectra at 4.2 K were taken using a regular Oxford Instruments cryostat. The *in situ* Mössbauer spectroscopic measurements were performed at 295 and 100 K. To record a spectrum at 100 K, the cell filled with the studied material was mounted in the hole of a copper bar immersed in a liquid-nitrogen-filled Dewar flask. The spectra were analyzed using routine software.

XPS measurements were made using an ESCALAB VG 220i-XL spectrometer (MgK_α exciting radiation, $h\nu$ = 1253.6 eV) with powder samples pressed on indium supports. Atomic concentrations were calculated from the integrated intensities of the Sn3d5/2 (E_b = 486.6 eV), Cr2p3/2 (E_b = 576.3 eV) and Y3d5/2 (E_b = 157.3 eV) peaks. High-resolution spectra were fitted and quantified using the AVANTAGE software provided by ThermoFischer Scientific, each spectrum being referenced to the Sn3d5/2 maximum at 486.6 eV.

Results and Discussion

*Mössbauer spectra of an $YCrO_3$ sample containing $^{119}Sn^{4+}$ in the bulk of crystallites (sample **1**)*

The spectrum at 295 K (Fig. 2a) consists of a broadened peak whose isomer shift value (δ = 0.08 mm s^{-1}) attests to the exclusively tetravalent nature of Sn. The significantly larger value of the width at half maximum (Γ = 1.15 mm s^{-1}), as compared to that of a reference $BaSnO_3$ sample ($\Gamma_{ref.}$ = 0.90 mm s^{-1}), is due to weak quadrupole interactions of $^{119}Sn^{4+}$ in the distorted perovskite structure of $YCrO_3$. The average value of the quadrupole splitting E_Q = 0.35 mm s^{-1} (Table 1), corresponding to the observed Γ value, is in qualitative agreement with the value E_Q = 0.46 mm s^{-1} [3] reported for Sn^{4+} in the somewhat more distorted structure of $LuCrO_3$.

At 4.2 K, a complex pattern of Zeeman splitting appears in the ^{119}Sn spectrum (Fig. 2b) which attests to the spin polarization of the electronic shell of Sn^{4+}

Table 1. Mössbauer-spectroscopic parameters of the ^{119}Sn probe located in the bulk (sample **1**) and on the surface (samples **2** and **2$_{ox}$**) of YCrO$_3$ polycrystals.

T, K	δ (mm s^{-1})	E_Q (mm s^{-1})	Γ (mm s^{-1})	H (kOe)	A (%)
Sample **1**:					
295	0.08 ± 0.03	0.35 ± 0.05	0.90 ± 0.05	–	100
4.2	0.11 ± 0.05		1.0 ± 0.1	80 ± 3	68 ± 5
	0.11 ± 0.05		1.0 ± 0.1	47 ± 5	12 ± 5
	0.11 ± 0.05		1.0 ± 0.1	17 ± 5	12 ± 5
	0.11 ± 0.05		1.0 ± 0.1	122 ± 5	8 ± 5
Sample **2** (*in situ* measurements):					
295	2.76 ± 0.04	1.95 ± 0.06	1.0 ± 0.1	–	86 ± 10
	~ 0				14 ± 5
100	2.82 ± 0.04	1.97 ± 0.06	1.1 ± 0.1	–	90 ± 5
	~ 0				10 ± 5
Sample **2$_{ox}$** (after exposure of sample **2** to air):					
295	0.06 ± 0.04	0.6 ± 0.1	1.1 ± 0.1	–	90 ± 10
	2.8 ± 0.1	2.0 ± 0.1	1.0 ± 0.1	–	10 ± 5
4.2	0.15 ± 0.05	0.7 ± 0.1	1.0 ± 0.1	–	70 ± 5
	0.15 ± 0.05		1.1 ± 0.1	35 ± 8	15 ± 5
	2.8 ± 0.1	2.0 ± 0.1	1.1 ± 0.1	–	15 ± 5

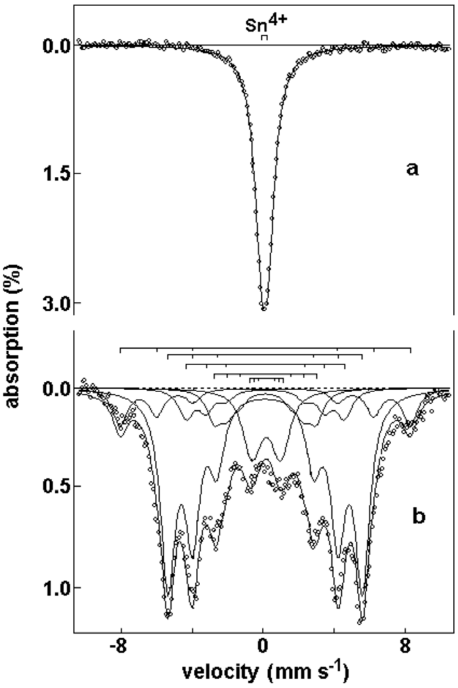

Fig. 2. ^{119}Sn Mössbauer spectra of sample **1**; T_{meas} = 295 K (a) and 4.2 K (b).

below T_N. The analysis of the spectrum shows that it can be represented by a superposition of a number of subspectra with different values of H (Table 1). The predominant contribution arises from the subspectrum corresponding to H = 80 kOe. This value is in close agreement with that reported in [2] for Sn^{4+} ions on the Cr^{3+} site in the bulk of YCrO$_3$ (at 10 K, H = 75 kOe). It should be noted that the sample studied in [2] was synthesized by annealing a mixture of Y$_2$O$_3$ and Cr$_2$O$_3$ which contained, besides the ^{119}SnO$_2$ additive, an equimolar amount of CaO to compensate the Sn^{4+} excess charge. So, the absence in [2] of any allusion to the occurrence of various ^{119}Sn subspectra allows us to account for the complexity of the spectrum in Fig. 2b by another Sn^{4+} charge compensation mechanism in the Ca^{2+}-free chromite structure. In fact, as the Cr^{3+} moments exhibit a G-type AF arrangement [10], each Cr^{3+} (and its isolated Sn^{4+} substituent) possesses, in this compound, six Cr^{3+} neighbors with parallel spins. This means that the partial contribution h from one neighboring Cr^{3+} to the effective H value at 4.2 K is expected to be *ca.* 13 kOe. Therefore, if the compensation of the Sn^{4+} excess charge in YCrO$_3$ involves the creation of vacancies $V_{\mathrm{Cr}^{3+}}$, as it was the case in Cr$_2$O$_3$ [11], some Sn^{4+} and $V_{\mathrm{Cr}^{3+}}$ sites may lead to the segregation of point defects. The Sn^{4+} ions concerned will thus possess a reduced number of magnetic neighbors, and new spectral components with lower values of H and multiples of 13 kOe will appear in the ^{119}Sn spectra. This expectation is in qualitative agreement with the data of a computer analysis of the spectrum of sample **1** at 4.2 K (Table 1). However, it is quite obvious that such segregations of point defects do not allow one to account for the presence of a sextet with $H \sim 120$ kOe, significantly greater than 80 kOe. On the contrary, the occurrence may be explained assuming that the compensation of the excess charge of some Sn^{4+} ions involves the formation of $V_{\mathrm{Y}^{3+}}$ yttrium vacancies. In fact, the appearance of $V_{\mathrm{Y}^{3+}}$ in the nearest surrounding of Sn^{4+} can change the average value of the angles θ of the concerned Cr(Sn)-O-Cr superexchange pathways. It was shown [2] that, with a decreasing ionic radius r of R^{3+}, the θ value decreases, and the π bonding (responsible for the spin polarization of Sn^{4+}) increases. Consequently, an increase of the H value is observed with decreasing r. Therefore, if there is a $V_{\mathrm{Y}^{3+}}$ vacancy in the vicinity of Sn^{4+} (which corresponds to the substitution of Y^{3+} for an atom with r = 0), the *local* average θ value is expected to be lower than 144.9°, the value reported in [12] for undoped YCrO$_3$. It has been shown [2, 13] that the dependence of H on θ may be approximated by a linear relation $H = a_0 + a_1 cos^2\,\theta$ with a_0 = 240 kOe and a_1 = -254 kOe. Accordingly, for the Sn^{4+} ions concerned the value of H = 120 kOe would correspond to the *local* average value of $\theta = 140°$.

*Mössbauer spectra of a tin-doped $YCrO_3$ containing Sn^{2+} on the surface of its crystallites (sample **2**)*

The *in situ* ^{119}Sn spectrum, recorded at 295 K after H_2 annealing of the tin-impregnated $YCrO_3$ sample (sample **2**), consists mainly of a quadrupole doublet and a weak residual absorption near $v \sim 0$ mm s^{-1} (Fig. 3a). Both the $\delta = 2.76 \pm 0.04$ mm s^{-1} and $E_Q = 1.95 \pm 0.06$ mm s^{-1} values, relative to the doublet (Table 1), are in fair agreement with those reported for Sn^{2+} ions on surface sites of $LuCrO_3$ (δ = 2.74 mm s^{-1} and E_Q = 1.94 mm s^{-1} [3]). The weak absorption observed near v = 0 mm s^{-1} attests to the presence of Sn^{4+} ions and thus points to the presence of a small amount of tin in the bulk of $YCrO_3$. An accurate determination of other Mössbauer spectrometric parameters of this component is prohibited by its too low spectral contribution.

According to [14], the features of the spectrum at 295 K clearly demonstrate the location of the large majority of tin ions on the surface of the crystallites. In fact, once Sn^{4+} ions appear at the interface, they are easily reduced by H_2 to the divalent state and, due to hybridized Sn^{2+} ($5s5p$) lone pair electrons, can occupy available low-coordination sites energetically unfavorable for Cr^{3+} and Y^{3+}. So the presence of Sn^{2+} diminishes the number of surface-located coordinatively unsaturated Cr^{3+} and Y^{3+} ions which results in the anomalously high stability of Sn^{2+} ions with respect to their further reduction to the metallic state. The surface localization of Sn^{2+} thus allows one to account for the at first glance surprising absence, in Fig. 3a, of the single-line peak of β-Sn (with δ = 2.56 mm s^{-1}), despite an H_2-annealing temperature as high as 900 °C. Finally, the surface-location of Sn^{2+} is in fair agreement with the results of an XPS analysis of the air-contacted sample **2**. The atomic ratio $\frac{[\mathrm{Sn}]}{[\mathrm{Cr}]+[\mathrm{Y}]}$ for a 2 – 3 nm thick surface layer is found to be 0.16. This value is about 100 times larger than the overall ratio calculated on the basis of the quantities of the reagents involved in the synthesis $\left(\frac{[\mathrm{Sn}]}{[\mathrm{Cr}]+[\mathrm{Y}]} = 0.0015\right)$.

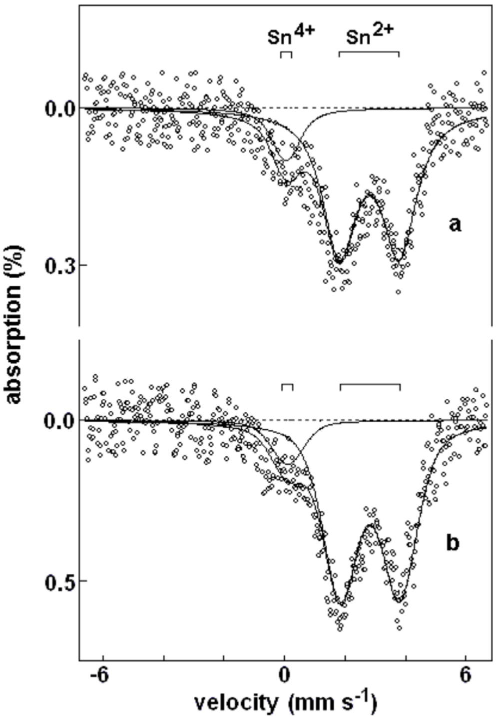

Fig. 3. ^{119}Sn Mössbauer spectra of sample **2**, recorded *in situ* in H_2; T_{meas} = 295 K (a) and 100 K (b).

The most interesting feature of the *in situ* spectrum at $T \sim 100$ K (Fig. 3b) is the fact that the peaks of the Sn^{2+} ions exhibit no Zeeman splitting, despite the rather low value of $\frac{T}{T_N} \sim 0.7$. The lack of spin polarization means that the Sn^{2+} ions possess a magnetically inactive surrounding and, consequently, an antiparallel orientation of the spins of their different Cr^{3+} neighbors. This conclusion is corroborated by Mössbauer spectroscopic measurements after a short-term exposure of sample **2** to air (sample $\mathbf{2_{ox}}$). In fact, the spectrum of sample $\mathbf{2_{ox}}$ at 295 K (Fig. 4a) reveals a rapid re-oxidation of the main part of the Sn^{2+} ions. This reaction probably involves only the attachment of an oxygen atom to the lone pair of electrons of a surface-located Sn^{2+}, without any significant change in the *cationic* surrounding of the oxidized Sn^{4+}. The validity of such an assumption has been experimentally proven for tin ions on the surface of Cr_2O_3 [15].

The comparison of the H values of Sn^{4+} ions located on sites with known surroundings in the bulk of $YCrO_3$ (sample **1**) with the H values relative to the "daughter" ($Sn^{2+} \rightarrow$)Sn^{4+} ions produced on the surface (sample $\mathbf{2_{ox}}$) reveals the peculiarities of the cation surroundings of the surface-located cations. The ^{119}Sn spectrum of sample $\mathbf{2_{ox}}$ at 4.2 K is shown in Fig. 4b. It suggests the presence of two kinds of Sn^{4+} ions. The large majority of them (Table 1) occupies sites with a magnetically inactive surrounding. Taking into account

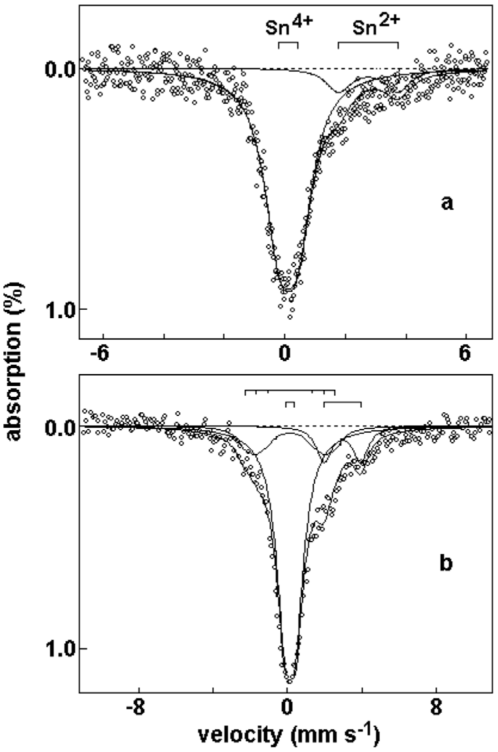

Fig. 4. ^{119}Sn Mössbauer spectra of sample $\mathbf{2_{ox}}$; T_{meas} = 295 K (a) and 4.2 K (b).

the very low value of $\frac{T}{T_N}$ = 0.03, this conclusion seems to be quite obvious. Consequently, on the surface, contrary to the bulk, the magnetically inactive Y^{3+} sites are mainly occupied by both the daughter Sn^{4+} and parent Sn^{2+} ions, in agreement with the lack of magnetic splitting in Fig. 3b.

However, as can be seen in Fig. 4b, a certain amount of spin-polarized Sn^{4+} ions (H = 35±5 kOe) is nevertheless present in sample $\mathbf{2_{ox}}$. As mentioned above, the sextet with H = 80 kOe represents Sn^{4+} on a Cr^{3+} bulk site possessing six Cr^{3+} neighbors. The spectral component with H = 35 kOe (Fig. 4b) is therefore to be attributed to Sn^{4+} located on surface Cr sites possessing only three Cr^{3+} neighbors. The lower value of H for the "daughter" Sn^{4+} ions concerned accounts for the lack of noticeable magnetic splitting for the "parent" $^{119}Sn^{2+}$ cations at 100 K (*cf.* Fig. 3b). In fact, contrary to the case of Sn^{4+}, the 5*s* orbitals of Sn^{2+} are formally filled. So, the 3*d*-5*s* transfer of spin density from Cr to Sn is strongly impeded for Sn^{2+}. This leads to a drastic decrease of the spin polarization of Sn^{2+} as compared to Sn^{4+}. For instance, the H value was found to be 2.5 times lower for Sn^{2+} on the surface of Cr_2O_3 [15] and about 13 times lower for Sn^{2+} in the bulk of α-MnS (containing both Sn^{2+} and Sn^{4+} ions on the sites with a similar cationic surrounding) [16]. Accordingly, for the value of 35 kOe, relative to the "daughter" Sn^{4+} (sample $\mathbf{2_{ox}}$), a value of H ranging from 14 to 3 kOe is to be anticipated at 100 K for the parent $^{119}Sn^{2+}$ (sample **2**). Such magnetic fields are too weak to noticeably affect the shape of a composite spectrum comprising a much more intense pure quadrupole doublet with very similar Mössbauer spectroscopic parameters.

Conclusions

The location of Sn^{4+} ions (0.3 at.-%) on Cr^{3+} sites in the bulk of $YCrO_3$ is shown to involve the formation of charge compensation vacancies of both chromium ($V_{Cr^{3+}}$) and yttrium ($V_{Y^{3+}}$). The occurrence of $V_{Cr^{3+}}$ in the nearest cationic surrounding of Sn^{4+} decreases its spin polarization while the presence of $V_{Y^{3+}}$ has the opposite effect. Upon annealing in H_2, reduction of Sn^{4+} to Sn^{2+} and stabilization of the latter on the surface sites becomes evident. The lack of spin polarization for the large majority of the Sn^{2+} ions at 4.2 K points to their location on Y^{3+} sites.

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