# Hyperfine interactions of $^{119}Sn^{2+}$ impurities in the surface layers of antiferromagnetic particles of $Cr_2O_3$

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An investigation of a system with 0.3 at. % of $Sn^{2+}$ in $Cr_2O_3$ by Mössbauer spectroscopy and electron spectroscopy for chemical analysis (ESCA) showed that during preparation of the samples the divalent-tin ions migrate to the surface of chromic oxide particles. Mössbauer spectra provide evidence that $Sn^{2+}$ impurity ions participate in exchange interactions with the antiferromagnetic matrix of $Cr_2O_3$. The geometry of the anionic environment of the $Sn^{2+}$ ions in the surface $Cr_2O_3$ layers corresponds to cationic positions in the orthorhombic phase of SnO. The electric field gradient at the $^{119}Sn^{2+}$ nuclei is negative, which confirms the bond hybridization model which Boyle *et al.* used to interprete the quadrupole interactions in compounds of divalent tin. The removal of $5s$-electrons upon oxidation of the $Sn^{2+}$ as a result of the adsorption of oxygen molecules is accompanied by a threefold increase of the hyperfine magnetic field at the nuclei of the impurity ions.

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## 1. INTRODUCTION

Mössbauer spectroscopy of the $^{119}Sn$ nuclei introduced as impurities in magnetically ordered dielectrics permits a study of the magnetic and structural characteristics of the nearest enviornment of the "Mössbauer probe" and yields information on the influence of covalency of chemical bonds on the spatial distribution of the spin density in the crystals studied. The most important class of magnetically ordered compounds, from the theoretical and practical viewpoint, are materials based on oxides of $3d$ transition metals. In research on such systems by the method of Mössbauer spectroscopy of $^{119}Sn$ nuclei, the tin impurity has invariably been introduced in the tetravalent state.

The employment of $^{119}Sn^{2+}$ as a Mössbauer diamagnetic probe in the case of oxides of transition metals was impossible up to now, because the radius of the $Sn^{2+}$ ions was too great and the valency state too unstable at the comparatively high temperatures necessary for preparing the samples. None the less, if $^{119}Sn^{2+}$ were successfully introduced into the compact oxide lattice, it is just the unsuitable parameters of the ion which would give grounds for expecting to obtain information about the crystal regions inaccessible to $^{119}Sn^{4+}$, and to investigate the influence of the electronic structure of impurity ions on the process whereby hyperfine magnetic fields are induced.

In this work we investigated the hyperfine interaction of $^{119}Sn^{2+}$ ions in antiferromagnetic $Cr_2O_3$ crystals. The choice of chromic oxide is explained by the fact that this compound, whose crystallographic and magnetic structure are well-known,[1,2] (space group R3c, antiferromagnetic ordering of the first kind, Neel temperature $T_N = 308$ K) is chemically stable under the reducing conditions needed to stabilize tin in the divalent state. In addition, this compound was recently investigated[5] by Mössbauer spectroscopy on $^{119}Sn^{4+}$ nuclei; this made possible a com-parison of the parameters of the hyperfine interactions for the two indicated valence states of the tin impurity ions.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Samples of $Cr_2O_3$: $^{119}Sn^{2+}$ were prepared by the following method: initially $Sn^{4+}$ ions (0.3 at.%, 90% enriched in $^{119}Sn$) were coprecipitated with $Cr^{3+}$ ions in the form of the hydroxide. After this the $Cr_2O_3$: $^{119}Sn^{4+}$ precipitate obtained was annealed in a hydrogen atmosphere first for 3 hr at 400°C (reduction of $Sn^{4+}$ to $Sn^{2+}$) and then for 16 hr at 1100°C (formation of macrocrystalline particles of $Cr_2O_3$). Annealing of the samples was carried out in a reactor fitted with a thin-walled quartz cell permitting performance of Mössbauer measurements without bringing the sample in contact with air. The degree of crystallinity of the sample was monitored by x-ray phase analysis.

The Mössbauer spectra were obtained with a spectrometer of the electrodynamic type operating in the constant acceleration mode. The samples studied served as absorbers. The source, instead of the stannate usually employed, was an Ag:3%Sn alloy (isomer shift relative to a source in the form of $BaSnO_3$ was $\delta = +2.20 \pm 0.05$ mm/s; widths of emission lines $\Gamma = 0.35 \pm 0.05$ mm/s). This increased the resolution by decreasing the Doppler velocity range needed to measure the spectra of $^{119}Sn^{2+}$:$Cr_2O_3$.

The ESCA spectra were obtained with a Vacuum Generators ESCA III spectrometer, the exciting radiation being the $K\alpha$ line of Al ($h\nu = 1486.6$ eV). The samples studied, compressed on a metal grid, did not undergo any additional processing before insertion into the analyzer.

Cleaning of the surface of the particles of $Cr_2O_3$ was accomplished by bombardment of the compressed powders with a beam of $Ar^+$ ions (accelerating voltage

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2 kV, current 10 $\mu A$). The concentration of tin $N_{Sn}/N_{Cr}$ was determined by measuring the ratio of the areas $A$ of the $Sn3d_{5/2}$ peaks (binding energy $E_L = 493$ eV) and $Cr2p_{3/2}$ ($E_L = 576$ eV), with compensation for the effective photoionization cross section $\sigma$ and for the absorption of the electrons in the matrix.

$$\frac{N_{Sn}}{N_{Cr}} = \left(\frac{A}{\sigma\sqrt{E_c}}\right)_{Sn3d_{5/2}} \Bigg/ \left(\frac{A}{\sigma\sqrt{E_c}}\right)_{Cr2p_{1/2}},$$

where $\sigma(Sn3d_{5/2}) = 14.8$ b (Ref. 4), the kinetic energy $E_c(Sn3d_{5/2}) = 993$ eV and $\sigma(Cr2p_{3/2}) = 7.69$ b (Ref. 4) and $E_c(Cr2p_{3/2}) = 910$ eV.

## 3. LOCALIZATION OF $^{119}Sn^{2+}$ IMPURITY IONS IN THE SURFACE LAYERS OF $Cr_2O_3$

The Mössbauer spectrum of a sample annealed in a hydrogen atmosphere at 1100°C, measured in the paramagnetic region at $T = 310°$K (Fig. 1a), is a doublet with an isomer shift $\delta/Sn(Ag) = +0.73 \pm 0.02$ mm/s and quadrupole splitting $\Delta = 2.08 \pm 0.04$ mm/s. These parameters, which unambiguously indicate that the tin impurity ions are in the divalent state, agree within the limits of the measurement error with the values of $\delta$ and $\Delta$ obtained for $^{119}Sn^{2+}$ in the ortho-rhombic phase of SnO (Ref. 5). The comparison made by Boyle et al.[5] of the values of the isomer shifts and quadrupole splittings of a number of compounds of divalent tin has made possible the conclusion that the nearest environment of $Sn^{2+}$ in the orthorhombic phase of SnO consists of a triangle of equidistant oxygen atoms, located on one side of the tin atom, just as in the case of $Pb^{2+}$ ions in orthorhombic PbO. In this structure three hybrid $sp^3$ orbitals of the metal atom are directed towards the nearest oxygen atom, while the fourth (non-bonding) orbital is populated by an un-shared electron pair which determines the electric field gradient (EFG) at the nuclei of the tin atoms. Since the appearance of induced magnetic fields at $T \lesssim T_N$ (Fig. 1b) excludes the possibility of formation of an SnO microphase, the indicated agreement of the values of $\delta$ and $\Delta$ indicates that the tin impurity ions in distinction from the $Cr^{3+}$ ions that occupy octahed-ral positions in the $Cr_2O_3$ structure, have a coor-
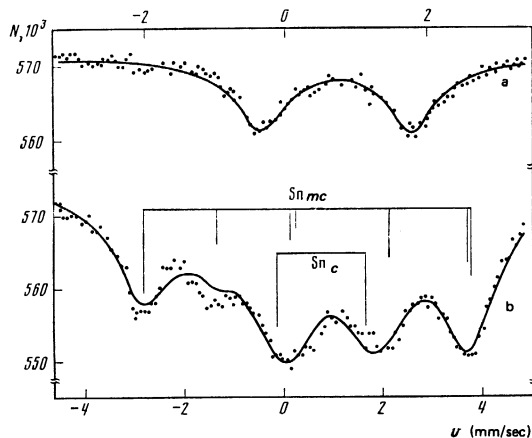
dination number three, as in the case of orthorhom-bic SnO.

This result serves as a first indication that the $Sn^{2+}$ ions must be located on the surface of the $Cr_2O_3$ par-ticles: the formation of a defect corresponding to the absence of three atoms of oxygen in the nearest environment of an impurity inside a $Cr_2O_3$ microcrystal is impossible, if account is taken of the structural distortions caused by such a defect.

The proposed localization of the $Sn^{2+}$ ions on the surface of the $Cr_2O_3$ particles is confirmed by the in-stantaneous oxidation to $Sn^{4+}$ ($\delta(BaSnO_3) = 0.0$ mm/s; $\Delta = 0.0$ mm/s) which occurs upon contact of the sam-ples with air at room temperature, at which such a quick diffusion of oxygen atoms into the interior of the $Cr_2O_3$ crystals is impossible.

Direct proof of the localization of the tin in the sur-face layers of $Cr_2O_3$ was obtained by measuring the ESCA spectra, which yielded the impurity content at a distance from the surface not exceeding about 20 Å (the mean free path of the electrons between two con-secutive inelastic collisions). The ESCA spectra of a crystalline sample ($T_{ann} = 1100°C$) obtained before the ionic bombardment showed that in the surface layers of $Cr_2O_3$ contained forty times more tin (11.5 at.%) than initially (0.3 at.%). The tin content in the amor-phous sample ($T_{ann} = 400°C$) turned out to be 0.7 at.%. This indicates the onset of $Cr_2O_3$ crystallization of the not yet observed in the x-ray photographs and producing only a negligible disturbance of the uniform distribution of the impurity. The observed change in the ratio $N_{Sn}/N_{Cr}$ as a function of bombardment time $t$ (see Table I) also confirms the initial uniformity of the tin distribution in the amorphous sample. In the case of a crystalline sample, on the contrary, bombardment by $Ar^+$ ions leads immediately to removal of an ap-preciable part of the tin atoms, after which the im-purity content decreases slowly to 1.4 at.% ($t = 1.5$ h). Thus, the observed change of the ratio $N_{Sn}/N_{Cr} = f(t)$ indicates once more that crystallization leads to a localization of tin on the surface of $Cr_2O_3$ particles. The reduction of the rate of decrease of the tin con-centration upon bombardment of the crystalline sample is governed by the texture of the investigated powder.

## 4. MAGNETIC DIPOLE AND QUADRUPOLE HYPERFINE ELECTRIC INTERACTIONS OF $^{119}Sn^{2+}$ IMPURITY IONS

The low-temperature Mössbauer spectrum gives evi-dence of the simultaneous presence of magnetic and



FIG. 1. Mössbauer absorption spectra of $^{119}Sn^{2+}$ impurity ions in $Cr_2O_3$; a) $T = 310°$K; b) $T = 77°$K; source: $^{119}Sn(Ag)$.

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quadrupole interactions, of comparable magnitude, for $^{119}Sn^{2+}$ ions localized in the surface layers of antiferromagnetic $Cr_2O_3$ particles. Therefore, to interpret the spectrum it is necessary to use the full Hamiltonian of the hyperfine interaction. The Hamiltonian may be represented in the following form, in a system of coordinate axes coinciding with the principal axes of the tensor of the electric field gradient

$$\mathcal{H} = -g\mu_N H\{I_z\cos\theta + (I_x\cos\varphi + I_y\sin\varphi)\sin\theta\}$$
$$+ \frac{eQV_{zz}}{4I(2I-1)}\{3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)\}, \tag{1}$$

where $g$ is the nuclear $g$ factor, $\mu_N$ is the nuclear magneton, $Q$ is the quadrupole moment of the nucleus, $e$ is the charge of a proton, $V_{zz}$ is the principal component of the tensor of the EFG, $I$ is the spin of the nucleus, $I_x$, $I_y$, and $I_z$ are the operators of the projections of the angular momentum, $\theta$ and $\varphi$ are the polar and azimuthal angles determining the orientation of the hyperfine magnetic field, $H$, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the assymmetry parameter of the EFG tensor. The components of the EFG tensor are chosen such that $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$ ($0 \leq \eta \leq 1$).

The eigenvalues and eigenvectors of the Hamiltonian [Eq. (1)] were calculated with a computer using the following parameters: $R = eQV_{zz}/2g\mu_N H$ (where $g$ is the nuclear $g$ factor for the state $I = 3/2$), $\theta$, $\varphi$, and $\eta$. The positions of the lines in the Mössbauer spectrum were determined as the difference between the eigenvalues of the Hamiltonian for $I = 3/2$ and $I = 1/2$; the components of the eigenvectors were used to calculate the relative intensities of the corresponding transitions.

A preliminary analysis based on a comparison of the experimental spectrum with theoretical diagrams[6] showed that the low-temperature spectrum of $^{119}Sn^{2+}$ contained besides the composite hyperfine structure of $Sn_{mc}$ the additional doublet of $Sn_c$, whose parameters are close to the values of $\delta$ and $\Delta$, determined for the system $^{119}Sn^{2+}$:$Cr_2O_3$ at $T > T_N$. Inasmuch as lowering the impurity concentration to 0.2% did not decrease the contribution of "non-magnetic" $Sn^{2+}$ ions, the Hamiltonian [Eq. (1)] was initially employed to obtain only the lateral sections of the spectrum, which were not distorted by the presence of the doublet. This yielded the ratio of "magnetic" to "non-magnetic" tin, $Sn_{mc}/Sn_c \approx 2.5$.

Subsequent reduction of the experimental spectrum as the sum of the composite hyperfine structure and the doublet gave the following optimum combination of parameters determining the state of the $^{119}Sn^{2+}$ ions participating in the exchange interactions:

$$R = +2.5, \quad \theta = 90°, \quad \varphi = 90°, \quad \eta = 0.15;$$
$$H_{Sn^{2+}}(77\ K) = 38\pm1\ kOe; \quad eQV_{zz} = +3.6\pm0.3\ mm/sec.$$

Bearing in mind the negative value of the quadrupole moment $Q_{3/2}$ (Ref. 5), the positve sign of the constant quadrupole coupling signifies that $V_{zz}$ is also negative for the $Sn^{2+}$ ions. This result confirms the corrections of the initial supposition of Boyle et al.[5] that the electron term makes the dominant contribution to the
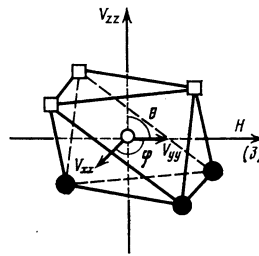


FIG. 2. Local environment of $^{119}Sn^{2+}$ impurity ions on the surface of $Cr_2O_3$ crystallites. O—tin, ●—oxygen, □—oxygen vacancy.

value of the EFG at the $Sn^{2+}$ nuclei in the structure of orthorhombic SnO.

The obtained hyperfine-interaction parameters allow us to represent in the following manner the transition from the normal octahedral positions occupied by the $Cr^{3+}$ ions in the $Cr_2O_3$ lattice to the positions of the surface $Sn^{2+}$ ions, which are typical of orthorhombic SnO. The presence of the trigonal distortion of the octahedral positions of $Cr^{3+}$ in the $Cr_2O_3$ structure (Ref. 1) requires examination of two possible cases:

1) the absence of three oxygen atoms forming one of the two equilateral faces of the octahedron;

2) the absence of three oxygen atoms belonging to one of the four isosceles faces of the octahedron.

Since the induced field $H$ must have the same direction as the magnetic moments of the $Cr^+$ ions (which are aligned along a threefold axis of the $Cr_2O_3$ crystals[2]), the first case leads to $\theta = 0°$ ($V_{zz}\|c\|H$); in the second case, in the presence of slight trigonal distortions the angle $\theta$ must be close to 60°. The value of $\theta$ determined from the Mössbauer spectrum is close to 90°, which makes the second case more probable. The observed deviation of the experimental value of $\theta$ from the angle 60° is not unexpected, if one takes into account the unavoidable displacement of the $Sn^{2+}$ ion from the center of the primitive octahedron towards the oxygen vacancies. This displacement permits the impurities to produce on the surface of the $Cr_2O_3$ a local environment characteristic of a cationic positions in orthorhombic SnO (Fig. 2).

Additional information on the state of tin in $Cr_2O_3$ surface layers was obtained by analyzing the Mössbauer spectra of $^{119}Sn^{4+}$ ions produced by the aforementioned instantaneous oxidation of $Sn^{2+}$ ions upon contact of the samples with air. One of the fundamental results, which will be treated in a separate article, is that removal of $5s$-electrons from the $Sn^{2+}$ ions was accompanied by a threefold increase of the hyperfine magnetic field: $H_{Sn^{4+}}(77°K) = 110\pm 5$ kOe. If one proposes that the cationic environment of the tin impurity ion does not undergo a substantial change when the surface oxygen atoms are joined, the observed increase in $H$ confirms the assumption[7] that the dominant role is played by the transfer of the spin density into the vacant $5s$-orbitals when the hyperfine magnetic field is produced at the nuclei of $^{119}Sn^{4+}$ ions in magnetically-ordered dielectrics.

value of the quadrupole

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