HYPERFINE STRUCTURE OF THE MÖSSBAUER SPECTRA OF $^{119}Sn^{4+}$ IN Cr_2O_3

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Mössbauer studies of ^{119}Sn impurity nuclei introduced into antiferromagnetic oxides (α-Fe_2O_3 [1-4] and MnO [5]), indicated the presence of rather strong effective magnetic fields (H_{eff}) at the nuclei of the diamagnetic Sn^{4+} ions.

This paper reports results obtained for $^{119}Sn^{4+}$ in the antiferromagnetic oxide Cr_2O_3, which, like α-Fe_2O_3, has the structure of corundum ($R\bar{3}c$) but differs from α-Fe_2O_3 in having a smaller effective magnetic moment of the matrix cations ($\mu_{Fe_2O_3} = 5{,}92\,\mu_B$, $\mu_{Cr_2O_3} = 3{,}73\,\mu_B$).

Cr_2O_3 specimens were prepared by air roasting of freshly precipitated Cr(III) hydroxide containing an Sn^{4+} impurity (88% enrichment in ^{119}Sn). The formation of crystalline chromic oxide was established by X-ray diffraction.

The presence of hyperfine structure of $^{119}Sn^{4+}$ introduced into the crystal lattice of an antiferromagnetic oxide makes it possible to estimate the maximum solubility of the diamagnetic tin impurity from the time of appearance of the unsplit central line in the low-temperature spectra of ^{119}Sn as the tin concentration is increased. For Cr_2O_3, the solubility of Sn^{4+} was ~1 at.%.

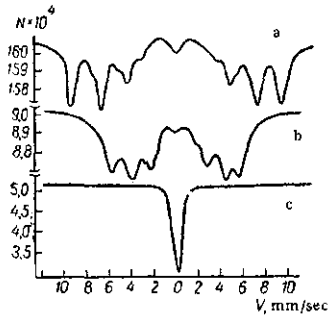

Fig. 1. Experimental curves of Mössbauer spectra of $^{119}Sn^{4+}$ in Cr_2O_3: a) T = 77°K; b) T = 293°K; c) T = 373°K.

Mössbauer Spectrum Parameters of $^{119}Sn^{4+}$ in Cr_2O_3

T °K	Chemical shift*, mm/sec	Quadrupole interaction**, mm/sec	H_{eff}, kOe
77	0,20 (0,12)	—0,50 (—0,90)	137 (100)
373	0,16 (0,06)	0,60 (1,4)	0 (0)

*With respect to $BaSnO_3$ at 295° K.
**The figures given are the difference of the distances between components 1, 2 and 5, 6 of the magnetic multiplet at $T < T_N$ and twice the distance between the components of the doublet at $> T_N$.

Much of the work was done on a coarse crystalline Cr_2O_3 specimen after annealing at 1000°C ($\bar{d}_{x-r} > 500$ Å) containing 0.5 at.% of Sn^{4+}.

The Mössbauer spectra were obtained on a constant-acceleration electrodynamic spectrometer. The source was Ba $^{119}SnO_3$ at room temperature. A resonance counter [6] was used as the detector.

Cr_2O_3 has a Neel temperature T_N = 307°K [7]. Accordingly, the spectrum of $^{119}Sn^{4+}$ does not have magnetic hyperfine structure at T_{meas} = 373°K. Cooling of the absorber to a temperature below T_N results in Zeeman splitting of the nuclear levels of the ground and first excited states of ^{119}Sn (Fig. 1). The basic parameters of the Mössbauer spectra are given in the table. The hyperfine-splitting pattern observed at a specimen temperature of 77°K corresponds to a magnetic field H_{eff} (77°) = 137 ± 1 kOe at the $^{119}Sn^{4+}$ nuclei.

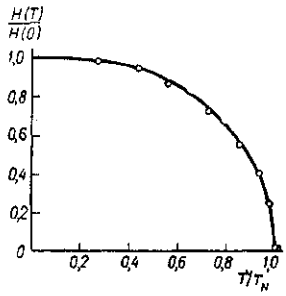

Fig. 2. Temperature variation of H_{eff} on $^{119}Sn^{4+}$ nuclei (the solid curve represents the Brillouin function for S = 3.2). The plotted points are the experimental values.

We note that in the case of the finely dispersed Cr_2O_3 specimen ($\bar{d}_{x-r}$ < 100 Å), the spectrum obtained at T_{meas} = 77°K was poorly resolved and had the much smaller value $H_{eff}(77°) \approx 100$ kOe. The observed decrease in the field is qualitatively consistent with theoretical data for the lowering of T_N in highly dispersed systems.

The hyperfine structure corresponding to $H_{eff}(77°) \sim 100$ kOe also appears in measurements with the coarse crystalline specimens. It has an intensity of about 20% of the main signal. The parameters of this spectrum are indicated in parentheses in the table. It is possible that in addition to the residual effect of the granule sizes, the secondary structure is due to interactions of the impurity-impurity type that weaken the magnetic field at the nuclei of atoms that have one of the magnetically active chromium ions in the immediate coordination sphere replaced by a tin ion.

The temperature dependence of H_{eff} stands in good agreement with the trend of the Brillouin function for S = 3/2 at T_N = 306°K.

Extrapolation of the experimental $H_{eff}(T)$ curve to low temperatures gives $H_{eff}(0)$ = = 138.5 ± 1 kOe, which is somewhat larger than the corresponding value for impurity tin atoms in an α-Fe_2O_3 matrix. Hence it follows that the magnetic fields at the nuclei of the impurity tin atoms in the two compounds with corundum structure that were studied do not correlate, as might have been predicted from the magnetic moments of the paramagnetic matrix ions.

It is known that because of differences in the electronic structure of the 3d-shells of the ions Cr^{3+} and Fe^{3+} ($l_g^0 t_{2g}^3$ and $l_g^2 t_{2g}^3$, respectively), Cr_2O_3 and α-Fe_2O_3 have somewhat different types of magnetic ordering even though the crystallographic structures are the same [8]. Direct comparisons of the $H_{eff}(0)$ of these compounds are therefore quite arbitrary.

Lack of data on the effects of superexchange interactions of various types on the effective magnetic fields at diamagnetic-impurity nuclei makes quantitative analysis of the behavior of H_{eff} difficult in compounds of the corundum type, where several types of exchange interaction differing in the angle of the cation-anion-cation bond take place simultaneously. However, comparison of our measurements with the results of [9], where a significant decrease in the magnetic field on the nuclei of impurity tin atoms was observed on the transition from an $LaFeO_3$ matrix to an $LaCrO_3$ matrix, indicates that the cation-anion-cation superexchange interaction, in which the l_g electrons of the magnetic cations participate, is of secondary importance in compounds with the corundum structure. It appears that the cation-cation interaction [10] due to overlap of the wave functions of the t_{2g} electrons is basic.

The high-temperature Mössbauer spectrum of $^{119}Sn^{4+}$ (Fig. 2) can be used to estimate the quadrupole interaction constant e^2qQ for $^{119}Sn^{4+}$ in Cr_2O_3. The value $e^2qQ = 0{,}6 \pm 0{,}1$ mm/sec was close to that found for $^{119}Sn^{4+}$ in α-Fe_2O_3 [3].

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