

# Anomalous behavior of the probability for a Mössbauer effect in $\text{SnO}_2$ doped with Fe

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The behavior of the probability for the occurrence of the Mössbauer effect  $f'$  in  $^{119}\text{Sn}$  nuclei in the system  $(1-x)\text{SnO}_2 - x\text{Fe}_2\text{O}_3$  at 295 K is studied. A minimum is observed on the curve of the concentration dependence  $f'(x)$ . The depth of this curve is  $\sim 17\%$  of  $f'(0)$ . The appearance of the minimum could be due to the perturbing effect of impurity defects on the phonon spectrum of the matrix.

In Refs. 1 and 2 a minimum was observed in the concentration dependence for the probability of the Mössbauer effect  $f'(x)$  in a number of tin-based binary alloys for contents of the impurity component  $x = 0.15\text{--}0.3$  at. %. To explain the appearance of a minimum, Brandt *et al.*<sup>1,2</sup> proposed a model according to which regions with a perturbed phonon spectrum, in which gradients of the amplitudes of vibrations of atoms of the matrix exist, are formed in the lattice of the alloy near impurity atoms. An analogous behavior of  $f'(x)$  was observed by Nikolaev *et al.*<sup>3</sup> and Baltrunas *et al.*<sup>4</sup> in systems of solid solutions  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  and  $(\text{PbSe})_{1-x}(\text{SnTe})_x$ , which are narrow-band semiconductors and which pass through a gapless state in the range of concentrations  $0.6 < x < 0.7$ . The appearance of a minimum on the  $f'(x)$  curve in the region  $x \sim 0.6\text{--}0.7$  was explained in Refs. 3 and 4 by a “softening” of the phonon spectrum, caused by a change in the electronic spectrum that accompanies a transition of the semiconductor to a gapless state.

It would be worthwhile to study such anomalies in the behavior of  $f'(x)$  in systems such as oxides which differ considerably in terms of their structure and properties from those studied in Refs. 1–4. For this purpose, we have investigated the behavior of  $f'(x)$  on  $^{119}\text{Sn}$  nuclei in polycrystalline specimens of the system  $(1-x)\text{SnO}_2 - x\text{Fe}_2\text{O}_3$  with different  $\text{Fe}_2\text{O}_3$  content.

We prepared the specimens using the procedure described in Ref. 5. According to data from x-ray phase analysis (XRPA), the diffraction pictures of specimens with  $x = 0.2\text{--}0.3$  mol % contain only reflections corresponding to the  $\text{SnO}_2$  phase, the diffraction pictures of specimens with  $x = 6$  and 11 mol % also exhibit reflections from the  $\alpha\text{-Fe}_2\text{O}_3$  phase. The total iron content in the system, after synthesis of the specimens, was refined with the help of a chemical analysis. It was established in Ref. 5 that superparamagnetic  $\alpha$ - and  $\gamma\text{-Fe}_2\text{O}_3$  inclusions, whose small size ( $\langle d \rangle \lesssim 50$  Å) does not permit observing them with the help of XRPA, can form in the system  $\text{SnO}_2\text{--Fe}_2\text{O}_3$ . For this reason, in order to analyze the phase composition of the specimens, we used the method of static magnetic susceptibility, which is sensitive to the appearance of magnetically ordered clusters in the system (the measurements were performed at the

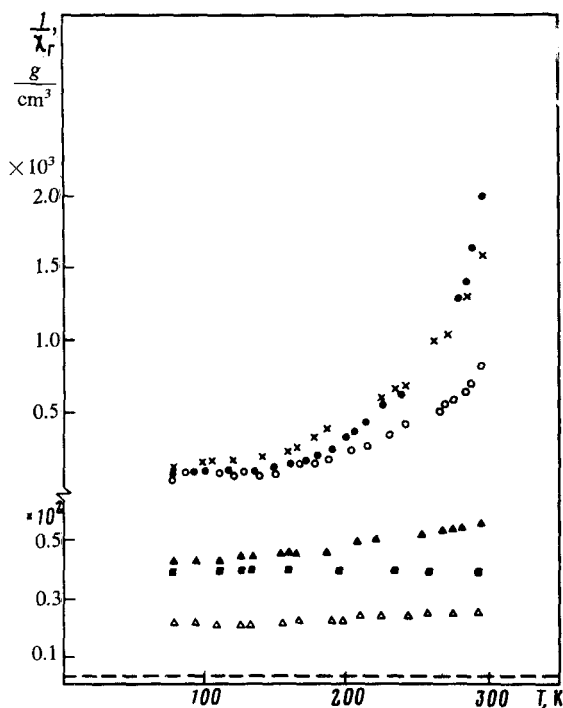


FIG. 1. Temperature dependence of the inverse bulk magnetic susceptibility in the system  $(1-x)\text{SnO}_2-x\text{Fe}_2\text{O}_3$  for the following values of  $x$  (mol %): 0.3 (●); 0.5 (×); 0.7 (○); 1.0 (▲); 1.5 (△); ■ is for pure  $\alpha\text{-Fe}_2\text{O}_3$ ; the dashed curve is for pure  $\gamma\text{-Fe}_2\text{O}_3$ .

Institute of General and Inorganic Chemistry of the USSR Academy of Sciences). Figure 1 shows the temperature dependences of the inverse bulk magnetic susceptibility  $1/\chi_T$ , measured for different  $x$ . It is evident from the behavior of  $1/\chi_T$  that Curie's law no longer holds for  $x = 0.3$  mol %. This is attributable to the fact that the system has, in addition to paramagnetic  $\text{Fe}^{3+}$  ions which replace  $\text{Sn}^{4+}$  ions in the  $\text{SnO}_2$  lattice, magnetically ordered clusters, whose contribution to  $\chi_T$  increases with increasing  $x$  and at  $x > 1$  mol % becomes dominant.

Mössbauer spectra of  $^{119}\text{Sn}$  were measured at 295 K with a  $\text{Ba}^{119\text{m}}\text{SnO}_3$  source and were analyzed on a BESM-6 computer using the standard program. The effective thickness of the absorbers for  $^{119}\text{Sn}$  was  $0.3 \text{ mg/cm}^2$ . The values of spectral parameters such as the isomeric shift, quadrupole splitting, and line width are identical for all specimens, within the limits of accuracy of the analysis, and are typical for  $\text{SnO}_2$ . We determined the probability of the Mössbauer effect  $f'$  from the normalized area  $S$  under the absorption curve, analogously to the procedure described in Ref. 2. We performed two to three measurements for each specimen, and for some specimens we prepared additional absorbers. The measurements with the  $^{57}\text{Fe}$  nuclei showed that the iron in the system was found only in the  $\text{Fe}^{3+}$  state.

The variation in the area  $S \propto f'$  as a function of the  $\text{Fe}_2\text{O}_3$  concentration is shown in Fig. 2. We see a distinct minimum on the curve  $S(x)$  at  $x = 0.5$  mol %, whose depth

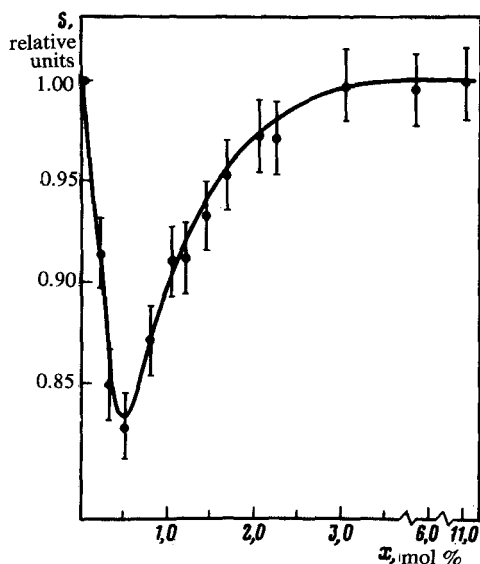


FIG. 2. The area  $S$  under the curve for the Mössbauer spectrum as a function of  $x$  for the system  $(1-x)\text{SnO}_2-x\text{Fe}_2\text{O}_3$ .

is  $\sim 17\%$  of  $S(0)$ . This decrease in  $f'$  clearly shows that the force constants of the  $\text{SnO}_2$  crystal lattice decrease in strength and that the vibration amplitudes of tin atoms increase. It is well known that significant changes in the probability of the Mössbauer effect can be observed at first-order phase-transition points, when either the lattice parameter or the crystal structure change discontinuously. Since the structural type of the matrix does not change in our case, i.e., there is no first-order phase transition, the minimum on the  $S(x)$  curve can only be related to the formation of regions with a perturbed phonon spectrum near the impurity defects, as discussed in Refs. 1 and 2. Here we can suggest the existence of two types of defects: 1) point defects—impurity  $\text{Fe}^{3+}$  ions, which replace the  $\text{Sn}^{4+}$  ions in the  $\text{SnO}_2$  structure, and 2) volume defects—iron-containing clusters, which are incorporated coherently into the  $\text{SnO}_2$  structure.

A more detailed analysis of the nature of the minimum requires a knowledge of the concentration of the impurity  $\text{Fe}^{3+}$  ions in the  $\text{SnO}_2$  structure and the Fe concentration in the clusters a subject of our future investigations.

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