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A Mössbauer Study of the Valence States of ^{119}Sn after the EC Decay of ^{119}Sb in Antimony and Tellurium Iodides

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Synopsis. The ^{119}Sn-Mössbauer emission spectra of $^{119}SbI_3$ and $^{119m}TeI_4$ sources showed the formation of Sn(II) and Sn(IV) species after the EC decay of ^{119}Sb in the matrices.

The measurement of the Mössbauer emission spectra enables one to estimate the chemical species produced by nuclear decay in solids.[1] In previous papers,[2–4] we reported a series of studies of ^{119}Sn after the EC decay of ^{119}Sb in metals, oxides, and chalcogenides of antimony and tellurium. This paper will describe an extension of these studies to iodides.

The 38.0 hr ^{119}Sb populates the 23.8 keV Mössbauer level of ^{119}Sn by 100% EC decay. The resonant γ-rays emitted from the level provide useful information on the electronic state of the ^{119}Sn atoms in the solid after the decay. We measured the Mössbauer emission spectra of ^{119}Sn arising in antimony iodide labeled with ^{119}Sb and also those of ^{119}Sn produced by the successive EC decays of 4.7 day ^{119m}Te *via* ^{119}Sb in tellurium iodide.[5]

The procedures for producing the source nuclides and for preparing the ^{119}Sb metal and $^{119m}TeO_2$ were reported elsewhere.[4,6,7] The $^{119}SbI_3$ sources were prepared by reacting the ^{119}Sb metal powder with iodine in refluxing toluene. The product was purified by repeated sublimation in a vacuum at 145 °C, yielding the iodide in the orange modification. The $^{119m}TeI_4$ samples were obtained by evaporating a solution of $^{119m}TeO_2$ in concd hydriodic acid over P_2O_5, SiO_2, and CaO under reduced pressure. The residue was thoroughly ground and then dried over fresh P_2O_5, SiO_2, and CaO in a vacuum until a constant weight ($\pm$0.1%) was attained. The source materials were identified by the Debye-Scherrer patterns, while their purity was checked by the titrimetrical determination of the component elements.

The ^{119}Sn-Mössbauer emission spectra of the iodides were measured against a $BaSnO_3$ absorber (0.9 mg ^{119}Sn/cm^2) by means of a conventional spectrometer with a transducer operated in the constant acceleration mode. Both the source and absorber were maintained at the temperature of liquid nitrogen in a cryostat. The 23.8 keV γ-rays were detected with a 2 mm NaI scintillator through an 80 μm Pd critical absorber for Sn KX-rays. In the case of the $^{119m}TeI_4$ samples, the change in the spectra with the time was followed until a constant value was obtained for the Sn(II)-to-Sn(IV) line-intensity ratio, so that the contribution of the ^{119}Sb arising from ^{119m}Te during the preparation of the samples was eliminated. The data were processed on the FACOM 230—60 and 75 computers of the Institute.

Typical spectra obtained are given in Fig. 1. The Mössbauer parameters of the emission lines, as determined by least-squares fitting, are summarized in Table

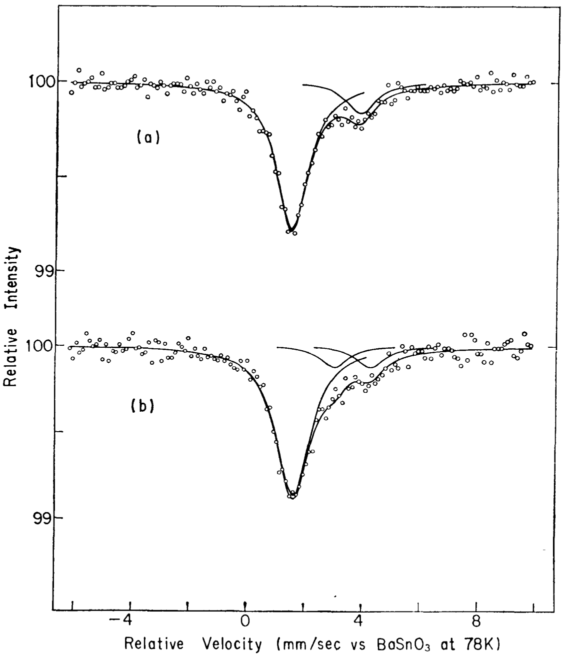

Fig. 1. ^{119}Sn-Mössbauer emission spectra of (a) $^{119}SbI_3$ and (b) $^{119m}TeI_4$ at 78 K against $BaSnO_3$ at 78 K. (In the abscissa a velocity of approach is taken negative.)

TABLE 1. MÖSSBAUER PARAMETERS OF THE EMISSION SPECTRA OF ^{119}Sn IN $^{119}SbI_3$ AND $^{119m}TeI_4$ AND OF THE ABSORPTION SPECTRA OF THE CORRESPONDING TIN IODIDES AT LIQUID NITROGEN TEMPERATURE

	Emission lines (this work)			Absorption lines (from the literature)			
Source materials	Isomer shift[a] (mm/s)	Quadrupole splitting (mm/s)	Assigned valence	Corresponding tin compounds	Isomer shift[b] (mm/s)	Quadrupole splitting (mm/s)	Ref.
$^{119}SbI_3$	1.50±0.05	—	Sn(IV)	SnI_4	1.55	—	8
	3.9 ±0.2	—	Sn(II)	SnI_2	3.88	—	9
$^{119m}TeI_4$	1.56±0.05	—	Sn(IV)	(see above)			
	3.5 ±0.3	1.4±0.3	Sn(II)	(see above)			

a) Relative to $BaSnO_3$ at 78 K. b) Relative to $BaSnO_3$.

1, together with the corresponding values of the absorption lines of tin iodides reported in the literature.[8,9]

As can be seen in Fig. 1(a), the emission spectra of ^{119}Sn arising in ^{119}SbI_3 consisted of two lines, which can be attributed to the Sn(IV) and Sn(II) states by comparing their isomer shifts with those of tin iodides (Table 1). Similarly, the ^{119m}TeI_4 sources gave emission lines in the Sn(IV) and Sn(II) regions. The computer fitting of the spectra with two Lorentzians resulted in a broad Sn(II) line accompanying the dominant Sn(IV) line. The further decomposition of the Sn(II) line into a symmetric doublet gave a quadrupole splitting value of 1.4 mm/s, as is shown in Fig. 1(b) and Table 1, giving rise to an improvement in the χ^2 value by 1.6%.

Since the EC decay is accompanied by a change in the atomic number, the ^{119}Sn atoms arising in the source materials must inevitably be in defect states associated with the local disturbance of the crystal lattice. The recoil energy accompanying the decay of ^{119}Sb is estimated to be much smaller than the threshold energy required to displace an atom from its normal lattice site, while the recoil energy of the EC decay of ^{119m}Te to ^{119}Sb is of the same order of magnitude as the displacement energy.

In SbI_3, each Sb is at the center of a nearly perfect octahedron of iodine atoms.[10] Therefore, the ^{119}Sn(IV) atoms arising in ^{119}SbI_3 may be expected to be in an electronic configuration different from that of SnI_4, in which tin atoms are surrounded by a practically regular tetrahedron of iodine atoms.[10] However, no significant difference was found between the isomer shift of the Sn(IV) emission line of ^{119}SbI_3 and that of the absorption line of SnI_4. Similarly, the isomer shift of the Sn(II) emission line is essentially identical with that of SnI_2. The crystal structure of TeI_4 seems not to have been determined yet. The powder X-ray diffraction pattern and the ^{125}Te-Mössbauer absorption spectrum of TeI_4[11] show that its structure is different from that of SnI_4, the site symmetry of the Te atom not being cubic. However, no significant difference was found between the isomer shift of the Sn(IV) emission line of ^{119m}TeI_4 and that of SnI_4. The quadrupole splitting observed for the Sn(II) line of the ^{119m}TeI_4 source is the only parameter found for the emission lines that is different from the corresponding value of the absorption line. SnI_2 has a monoclinic structure consisting of infinite $(SnI_3)_n^{n-}$ trigonal prisms, the coordination number of the tin atoms being seven.[12] The Mössbauer absorption spectrum of SnI_2, however, shows no resolvable quadrupole splitting.[9] The large quadrupole splitting of the Sn(II) emission line of ^{119m}TeI_4 suggests a much more distorted configuration of iodine ligands around the defect ^{119}Sn atom in the TeI_4 matrix.

It is interesting to compare the present results on iodides with those on oxides and chalcogenides reported previously.[4] In the series of antimony chalcogenides, the fraction of Sn(II) increased with the decrease in the electronegativity of the chalcogen ligand. The distribution ratio of ^{119}Sn between the Sn(II) and Sn(IV) states in ^{119}SbI_3 is closer to that of ^{119}Sb$_2$S$_3$ than to that of ^{119}Sb$_2$Te$_3$. This corresponds to the fact that the electronegativity of iodine is close to that of sulfur. The finding that the ^{119}Sn atoms were distributed between the Sn(II) and Sn(IV) states in ^{119m}TeI_4 presents an interesting contrast with the result for ^{119m}TeO_2, for which no Sn(II) species was observed. In ^{119m}TeO_2, the similarity of the crystal structures of TeO_2 and SnO_2 is considered to exclude the stabilization of ^{119}Sn as Sn(II). The absence of such an effect in TeI_4 as well as the lower electronegativity of iodine may have allowed the stabilization of a part of ^{119}Sn as Sn(II).

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