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^{119}Sn-Emission Mössbauer Studies on ^{119m}Te and ^{119}Sb in S, Se, and Te

Shizuko Ambe* and Fumitoshi Ambe
The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351-01

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The valence states of ^{119}Sn produced by the EC decay of diluted ^{119}Sb and ^{119m}Te chemically doped in S, Se, and Te were studied by emission Mössbauer spectroscopy. The Mössbauer spectra of S(^{119m}Te) and Se(^{119m}Te) consist of peaks ascribable to Sn(IV) and to Sn(II) surrounded by S or Se, respectively. The Mössbauer spectra of Te(^{119}Sb) samples show that, though a greater part of the ^{119}Sb atoms are dispersed in the Te matrix after coprecipitation and sublimation, upon slow recrystallization after fusion most of the dispersed ^{119}Sb atoms aggregate to form microcrystals of $^{119}Sb_2Te_3$.

We previously studied the chemical states of ^{119}Sn arising from EC-decaying ^{119m}Te and ^{119}Sb in binary compounds of Sn, Sb, and Te by ^{119}Sn-emission Mössbauer spectroscopy.[1—3] It was found that the valence states of ^{119}Sn after the decays are greatly influenced by the nature of the matrices. This paper first describes a similar study concerning ^{119}Sn arising from carrier-free ^{119m}Te, chemically introduced in elemental S and Se. The results are discussed in comparison with that on Te(^{119m}Te) metal.[1] In the second part of the paper, the chemical states of ^{119}Sn arising from ^{119}Sb in Te metal samples prepared by coprecipitation, sublimation, and slow recrestallization after fusion are described.

Experimental

The source nuclide, ^{119m}Te (4.86d), was produced by bombarding a metallic tin plate with 40-MeV α-particles accelerated in the RIKEN 160-cm cyclotron. The nuclide was separated from the Sn target by means of coprecipitation with Se metal. Carrier-free ^{119m}Te was separated from Se by means of anion exchange. Carrier-free ^{119}Sb (38.0 h) was obtained repeatedly by milking from ^{119m}Te, as was described in our previous paper.[4]

Carrier-free ^{119m}Te was coprecipitated with S formed by the reaction of Na_2SO_3 and Na_2S in an acid solution or with Se formed by the reduction of Se(IV) with $N_2H_4 \cdot 2HCl$ and Na_2SO_3 in an acid solution. The coprecipitation yield was almost 100% in both cases. The precipitates were purified by sublimation at 180 °C for S(^{119m}Te) and 280 °C for Se(^{119m}Te) under a reduced pressure of about 0.1 Pa. Almost all of the ^{119m}Te atoms were sublimated, depositing at the same band as S or Se on a cold part of the inner wall of the sublimation tube. The sublimates of S(^{119m}Te) and Se(^{119m}Te) were fused at 280 and 260 °C in an Ar atmosphere, respectively, and were slowly recrystallized.

Carrier-free ^{119}Sb was coprecipitated with Te in a yield of 40—90% by adding Cr^{2+} to a solution of ^{119}Sb(V) and Te(IV). The precipitate was sublimed at 1000 °C under a reduced pressure of about 0.1 Pa. At lower temperatures of 430—700 °C, only Te sublimed, leaving ^{119}Sb at the original position. Since the amount of Sb in the ^{119}Sb solution used for the study was 10^{-8} mole[5] and that of Te was 10^{-3} mole, the atomic ratio of Sb to Te was estimated to be of the order of 10^{-5}.

The S, Se, and Te prepared by the methods described above were found to be orthorhombic, hexagonal, and hexagonal by powder X-ray diffraction.

The ^{119}Sn-emission Mössbauer spectra of the samples were measured with a conventional Mössbauer spectrometer against a $BaSnO_3$ (0.9 mg ^{119}Sn/cm^2) absorber at 78 K. The 23.8-keV resonant γ-rays were detected with a 2 mm NaI scintillator, the Sn K X-rays being eliminated with an 80 μm Pd foil. Samples doped with ^{119m}Te were stored at liquid-nitrogen temperature before measurement, until a state of radioactive equilibrium had been established between ^{119m}Te and ^{119}Sb in the sample, in order to eliminate the contribution of ^{119}Sb arising from ^{119m}Te before and during sample preparation. The obtained data were analyzed using the FACOM M780 computer at our institute.

Results

^{119m}Te in Sulfur and Selenium. The emission Mössbauer spectra of S(^{119m}Te) and Se(^{119m}Te) samples are shown in Fig. 1. Since ^{119m}Te sources emit a number of γ-rays other than the Mössbauer one, the apparent intensity of the emission lines is small, resulting in poor statistics. Both spectra comprise a dominant peak and a shoulder. The shoulders are in the region for divalent tin. Fitting of the spectra with free parameters did not converge because of the poor statistics of the data. Accordingly, fitting was carried

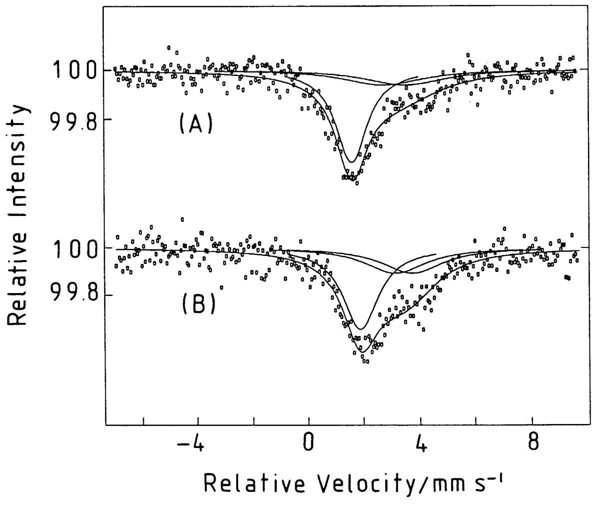

Fig. 1. Emission Mössbauer spectra of (A) S(^{119m}Te) and (B) Se(^{119m}Te). The relative velocity is given against $BaSnO_3$ at 78 K.

Table 1. Mössbauer Parameters of the Dominant Emission Lines of ^{119}Sn Arising from ^{119m}Te via ^{119}Sb in S and Se and Those of the Absorption Lines of the Related Compounds at Liquid-Nitrogen Temperature

Sample	Isomer shift mm s^{-1}	Quadrupole splitting mm s^{-1}	References
S(^{119m}Te)	1.6±0.1[a]	—	This work[b]
Se(^{119m}Te)	1.9±0.1[a]	—	This work[b]
SnS	3.16	0.8	[12]
SnS_2	1.20		[13]
SnSe	3.45	0.60	[14]
$SnSe_2$	1.27		[15]
0.5% Sn in Se	1.70		[9]

a) Relative to $BaSnO_3$ at 78 K. b) In the analysis of the spectra, the isomer shift and quadrupole splitting for the shoulder were fixed at the literature values of SnS or SnSe.

Table 2. Mössbauer Parameters of the Emission Lines of ^{119}Sn Arising from ^{119}Sb in Te and Emission and Absorption Lines of Related Compounds at Liquid-Nitrogen Temperature

	Isomer shift mm s^{-1}	Area %	Assigned species	References
Coprecipitated	2.85±0.05[a]	70	I ^{119}Sb in Te	This work
	3.4 ±0.1[a]	30	II $^{119}Sb_2Te_3$	
Sublimed	2.93±0.05[a]	80	I ^{119}Sb in Te	This work
	3.3 ±0.1[a]	20	II $^{119}Sb_2Te_3$	
Recrystallized after fusion	2.9 ±0.1	30	I ^{119}Sb in Te	This work
	3.45±0.05[a]	70	II $^{119}Sb_2Te_3$	
Te(^{119m}Te) metal	2.94±0.03[a]			This work[b]
$^{119}Sb_2Te_3$	3.39			[1]
SnTe	3.54			[2]
^{119}Sb metal	2.68			[1]

a) Relative to $BaSnO_3$ at 78 K. b) Remeasured by ourselves.

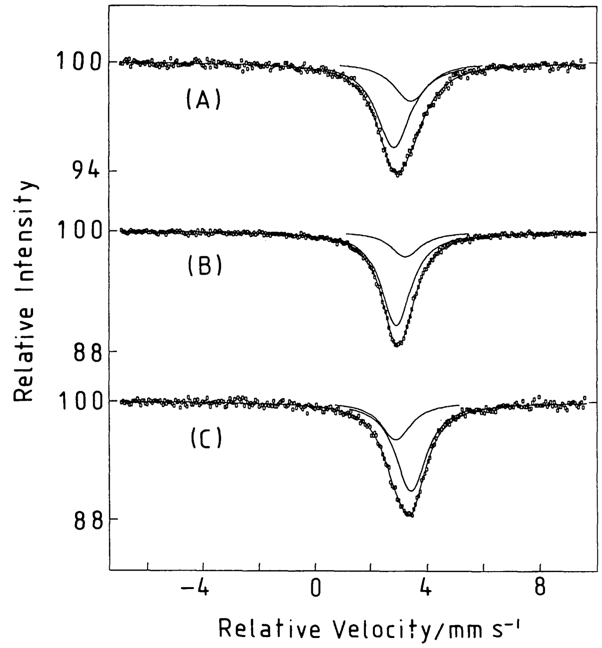

Fig. 2. Emission Mössbauer spectra of Te(^{119}Sb) (A) coprecipitated, (B) sublimed, and (C) slowly recrystallized after fusion. The relative velocity is given against $BaSnO_3$ at 78 K.

out by assuming for the shoulder a doublet with an isomer shift and quadrupole splitting fixed at the literature values of SnS or SnSe. The results are shown in Fig. 1 and Table 1. The spectrum of Te(^{119m}Te) is entirely different from that of S(^{119m}Te) and Se(^{119m}Te) and comprises a narrow single peak, as was described in our previous paper without detailed discussion.[1)]

^{119}Sb in Tellurium. The Mössbauer spectra of Te(^{119}Sb) samples (A) coprecipitated, (B) sublimed, and (C) slowly recrystallized after fusion are shown in Fig. 2. The apparently single lines are slightly asymmetric and satisfactory fitting required two Lorentzians (Fig. 2). The numerical results are summarized in Table 2, together with the Mössbauer parameters of related compounds. It can be seen from the table that all of the spectra consist of two common components: component I has a smaller isomer shift and II has a larger one, but in a different ratio.

Discussion

The maximum recoil energy associated with the EC decay of ^{119m}Te was estimated to be 44 eV, which is larger than the displacement energy in a solid (ca. 25 eV). Consequently, a part of the ^{119}Sb atoms are displaced from the original site of ^{119m}Te as a result of the decay. On the other hand, that of ^{119}Sb (1.5 eV) is much smaller than the displacement energy and the ^{119}Sn atoms arising from ^{119}Sb remain at the site of ^{119}Sb, unless it is chemically unfavorable for Sn. The estimation has been experimentally ascertained by emission Mössbauer studies on the binary compounds of Sn, Sb, and Te labeled with ^{119m}Te or ^{119}Sb.[2)]

Sulfur(^{119m}Te), Selenium(^{119m}Te), and Tellurium (^{119m}Te). Since the Mössbauer spectra of S(^{119m}Te) and Se(^{119m}Te) are distinctly different from that of Te (^{119m}Te),[1)] it is evident that ^{119m}Te is dissolved in elemental S and Se samples without segregation. Te enters Se or S substitutionally as a dilute impurity and is covalently bonded to two S or two Se in respective molecular units.[6–8)] Therefore, in our emission Mössbauer measurement, observations are made on the chemical states of ^{119}Sn arising via ^{119}Sb from ^{119m}Te situated at the substitutional site in S and Se.

The dominant peaks in the spectra of Fig. 1 are ascribed to Sn(IV), based on their isomer shifts. A large quadrupole splitting was observed in the ^{125}Te-Mössbauer spectra of $Te_{0.014}S_{0.986}$ and $Te_{0.02}Se_{0.98}$, where Te atoms are covalently bonded with two adjacent S or Se.[8)] However, no resolved splitting was observed for ^{119}Sn arising from the S(^{119m}Te) and Se(^{119m}Te) samples. The observation shows, even with due regard to the difference in nuclear quadrupole moments of ^{119}Sn and ^{125}Te, that local rearrangement of the chemical structure occurs resulting in a much more symmetric configuration than that for Te during the successive decays of ^{119m}Te to ^{119}Sn via ^{119}Sb. Although the isomer shifts are higher than those of SnS_2 and $SnSe_2$, the ^{119}Sn atoms are considered to be octahedrally coordinated with S and Se atoms, respectively. The high isomer shifts are ascribable to the fact that the ligand anions are coordinated to only one Sn(IV) ion. A similar observation is reported concerning crystalline Se doped with 0.5 at % of ^{119}Sn.[9)]

The shoulders observed in the spectra of S(^{119m}Te) and Se(^{119m}Te) are assigned to the Sn(II) species bonded to S and Se. The Mössbauer spectrum of ^{119}Sn (0.5 at %) in crystalline Se[9)] shows only a single line, suggesting that dilute Sn introduced in Se host is exclusively in the tetravalent state. Therefore, the shoulders observed for the S(^{119m}Te) and Se(^{119m}Te) samples are considered to originate in after-effects of EC decay. Namely, ^{119}Sb ions arising from ^{119m}Te are partly stabilized as ^{119}Sn(II) after decay. It is reported that ^{119m}Te implanted in Si shows a similar spectrum comprising a main substitutional peak and a shoulder ascribed to defect structures.[10)]

Te metal has a hexagonal structure comprising helical chains. An unbalanced p-electron distribution gives rise to a large quadrupole splitting in the ^{125}Te-Mössbauer spectrum.[7)] As we reported previously, however, Te(^{119m}Te) gives a single peak, indicating a single ^{119}Sn species in a highly symmetric local structure.[1)] Rots et al. reported a similar, but broader, spectrum for ^{119m}Sn implanted in a Te single crystal.[11)] They suggested that ^{119}Sn atoms are in a nearly octahedral environment with six Te atoms, four of them belonging to the adjacent chains. Our observation shows that even the ^{119}Sn atoms displaced from the original site of ^{119m}Te replace another Te atom and take such a configuration. The absence of the ^{119}Sn(IV) species in Te(^{119m}Te) metal is ascribed to the smaller electronegativity of Te compared with that of S and Se. A similar observation was made for ^{119}Sn arising from ^{119}Sb in antimony chalcogenides.[1)]

^{119}Sb in Tellurium Metal. Since ^{119}Sn is not displaced in the EC decay of ^{119}Sb, the lattice position of ^{119}Sb before decay can be determined on the basis of the Mössbauer parameters of the daughter ^{119}Sn. It is evident that ^{119}Sb atoms are not segregated as Sb metal in Te, since the isomer shifts of components I and II are much different from that of ^{119}Sb in Sb metal.[1)] Good agreement regarding the isomer shift of component I with that of Te(^{119m}Te) metal indicates that the corresponding ^{119}Sb atoms are present as isolated single atoms dispersed within the matrix. Component II is assigned to microaggregates of $^{119}Sb_2Te_3$ since its isomer shift is close to that of $^{119}Sb_2Te_3$.

The spectrum of a coprecipitated Te(^{119}Sb) sample (Fig. 2(A)) shows that ^{119}Sb atoms are dominantly dispersed as single atoms in the Te matrix, the rest forming microcrystals of $^{119}Sb_2Te_3$. The ratio is roughly retained after the process of sublimation (Fig. 2(B)). However, component II, assignable to $^{119}Sb_2Te_3$, increases markedly upon slow recrystallization after fusion of the coprecipitated or the sublimed sample. This shows that a much greater chance of aggregation is given to ^{119}Sb in the slower process of crystallization, compared with those of coprecipitation and sublimation.

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