April, 1991] Bull. Chem. Soc. Jpn., 64, 1289—1293 (1991)

Mössbauer Emission Study of Recoil ^{119}Sb and ^{119m}Te Atoms after Nuclear Decays and Reactions in SnS and SnSe

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

(Received December 4, 1990)

The chemical fates of ^{119}Sb and ^{119m}Te recoil atoms after p- and α-reactions in SnS and SnSe were studied by Mössbauer emission spectroscopy. The ^{120}SnS and ^{120}SnSe samples irradiated with protons gave a partly resolved asymmetric doublet ascribable to ^{119}Sn at the Sn site of the matrices. The α-irradiated ^{117}SnS and ^{117}SnSe samples gave emission spectra, drastically different from those of p-irradiated ^{120}SnS and ^{120}SnSe as well as that of α-irradiated ^{120}SnTe. The spectra are decomposable into three lines which are hardly assignable to any known chemical species of Sn and S or Se. Two of the lines are assigned to a doublet of divalent ^{119}Sn in the Sn site of SnS or SnSe with a nearby defect on the basis of their behavior on thermal annealing. The other line is ascribed to tetravalent ^{119}Sn in a defect structure.

The defect structures created in metals, semiconductors, and chemical compounds by energetic atoms have been extensively studied by hyperfine techniques.[1—10] However, the physical and chemical factors determining the final states of the atoms are not yet fully understood, especially concerning the last matrices. We previously reported a Mössbauer spectroscopic investigation of the ^{119}Sn atoms produced by nuclear-reaction and decay sequences ($^{120}\mathrm{Sn}(p,2n)^{119}\mathrm{Sb} \xrightarrow{\mathrm{EC}} {}^{119}\mathrm{Sn}$ and $^{117}\mathrm{Sn}(\alpha,2n)^{119m}\mathrm{Te} \xrightarrow{\mathrm{EC}} {}^{119}\mathrm{Sb} \xrightarrow{\mathrm{EC}} {}^{119}\mathrm{Sn}$) in SnTe.[11,12] In the matrix, the recoil ^{119}Sb atoms were found to be stabilized at both the Sn and Te sites.

In the present work, a similar investigation of the recoil atoms produced by nuclear reactions and decays in SnS and SnSe is described.[13] Although the results concerning SnS and SnSe were similar to each other, they were drastically different from that on SnTe. The ^{119}Sn atoms arising from ^{119}Sb atoms produced by the proton reaction were found exclusively at the Sn sites of SnS and SnSe, while those from ^{119m}Te after the α-reaction were found in defect states not observed in SnTe. The results are discussed in terms of the chemical properties of both the recoil atoms and the matrices.

Experimental

Tin isotopes enriched in ^{120}Sn or in ^{117}Sn and consequently depleted in ^{119}Sn (^{120}Sn 98.39% and ^{119}Sn 0.39% or ^{117}Sn 89.2% and ^{119}Sn 1.12%) were used for the preparation of both SnS and SnSe samples in order to reduce the resonant self-absorption of Mössbauer γ-rays in the samples. Crystalline ^{120}SnS and ^{117}SnS were prepared by the vacuum sublimation of amorphous tin sulfide, obtained by a reaction of H_2S gas on tin(II) ions in an aqueous solution. The samples of ^{120}SnSe and ^{117}SnSe were prepared by fusing a stoichiometric mixture of ^{120}Sn or ^{117}Sn metal with selenium under an Ar stream. The samples were examined by powder X-ray pattern and Mössbauer absorption measurements on the ^{119}Sn contained in them by a minute fraction.

Sample powder (50—100 mg cm^{-2}) pressed onto an aluminum plate was irradiated in a target chamber filled with flowing helium gas with 15-MeV protons or 32-MeV α-particles accelerated by the RIKEN 160 cm cyclotron. In the case of protons, irradiation with a beam of about 2.5 μA cm^{-2} was continued for several hours. For α-particles, the corresponding values were 0.5—0.6 μA cm^{-2} and 10—12 h. The targets were thin enough to let the bombarding particles pass through them, so that the intense energy dissipation of the particles near the end of their tracks did not occur in the samples, but in the aluminum backing. The backside of the aluminum plate was cooled directly with water during irradiation. After irradiation the samples were left standing at ambient temperature for 10—20 h, allowing short-lived nuclides to decay. Although neither the bulk temperature of the samples during irradiation nor the local temperature of the end point of the energetic recoil atoms were measurable, the effects of thermal annealing showed that the bulk temperature were less than 100 °C, and that the effect of local heating along the track of the recoil atoms was not serious, if any. The Mössbauer absorption spectra of the irradiated samples showed no trace of radiation damage. Annealing and fusion of the irradiated samples were carried out under an Ar atmosphere.

The Mössbauer emission spectra of the samples were measured against a $BaSnO_3$ (0.9 mg ^{119}Sn cm^{-2}) absorber, both being kept at liquid-nitrogen temperature. Measurements of the α-irradiated samples were performed after radioactive equilibrium had been attained between ^{119m}Te and ^{119}Sb. The spectra were least-squares fitted with lines of a Lorentzian shape using a FACOM M380 computer in our institute.

Results

The obtained emission Mössbauer spectra are shown in Figs. 1—5. The results of fitting are summarized in Table 1. The isomer shift is given relative to $BaSnO_3$ at room temperature.

The ^{119}Sn atoms produced in ^{120}SnS and ^{120}SnSe irradiated with protons gave a partly resolved asymmetric doublet, as can be seen in Figs. 1(A) and (B).

The emission spectra of ^{119}Sn in α-irradiated ^{117}SnS and ^{117}SnSe were complex (Figs. 2(A) and 3(A)), being completely different from those of p-irradiated ^{120}SnS and ^{120}SnSe sources. They were decomposable into

Table 1. Mössbauer Parameters of ^{119}Sn Arising from ^{119}Sb and ^{119m}Te in *p*- and α-Irradiated SnS and SnSe at Liquid Nitrogen Temperature. Errors for the Isomer Shift and Quadrupole Splitting are Estimated to be 0.05—0.1 mm s^{-1} for Large Peaks and 0.1—0.2 mm s^{-1} for Small Ones.

Samples	Annealing[a]	Isomer[b] shift	Quadrupole splitting	Relative area
		mm s^{-1}	mm s^{-1}	%
p-Irradiated ^{120}SnS	None	3.11	0.94	100
α-Irradiated ^{117}SnS	None	0.84		20
		3.10	1.66	80
	100 °C, 1 h	0.95		23
		3.18	1.55	77
	200 °C, 1 h	1.10		23
		3.27	1.22	77
	600 °C, 1 h	3.13	0.93	100
p-Irradiated ^{120}SnSe	None	3.27	0.79	100
α-Irradiated ^{117}SnSe	None	0.89		30
		3.16	1.73	70
	100 °C, 1 h	0.91		28
		3.18	1.50	72
	200 °C, 1 h	0.91		4
		3.04	1.10	96
	600 °C, 1 h	3.21	0.83	100

a) In an Ar stream. b) Relative to BaSnO$_3$ at room temperature.

three Lorentzian lines (designated as Line 1, 2, and 3 from the left to the right). Remarkable changes in the position and in the relative intensities of each line were observed upon thermal annealing of the irradiated samples, as can be seen in Figs. 2(B)—(D) and 3(B)—(D). In both cases of ^{117}SnS and ^{117}SnSe, Line 1 completely vanished upon annealing at 600 °C. Upon elevating the annealing temperature, the relative intensities of Lines 2 and 3 increased in parallel and the two lines shifted closer to each other, their

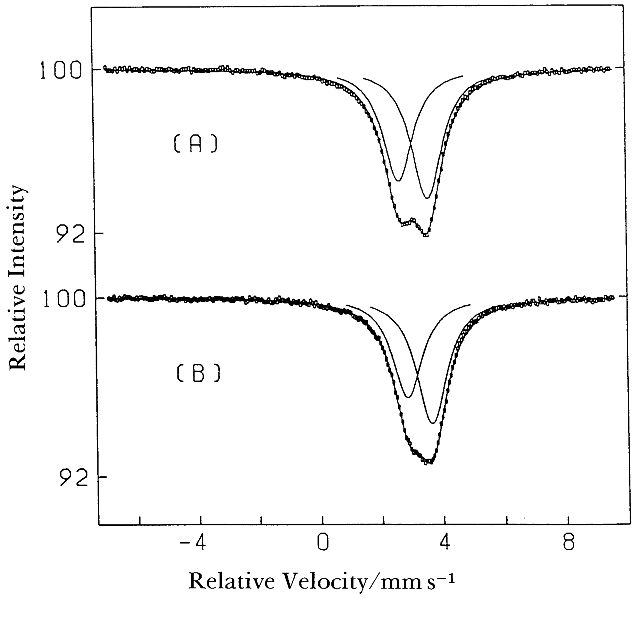

Fig. 1. Mössbauer emission spectra of ^{119}Sb→^{119}Sn in *p*-irradiated (A) ^{120}SnS and (B) ^{120}SnSe (measurement at liquid nitrogen temperature).

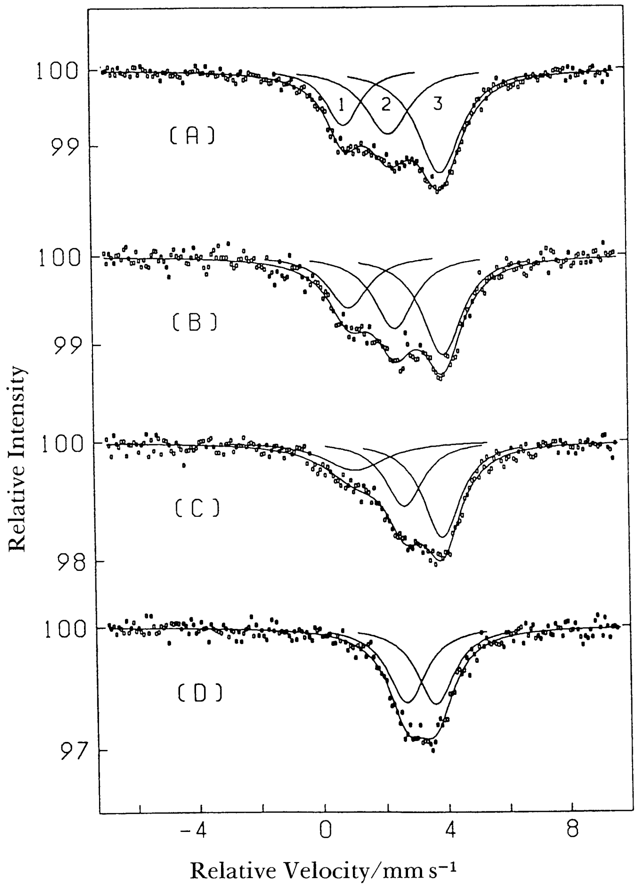

Fig. 2. Mössbauer emission spectra of ^{119m}Te→^{119}Sb→^{119}Sn in α-irradiated ^{117}SnS (measurement at liquid nitrogen temperature). (A) As irradiated, (B) after 1 h annealing at 100 °C, (C) after 1 h annealing at 200 °C, and (D) after 1 h annealing at 600 °C.

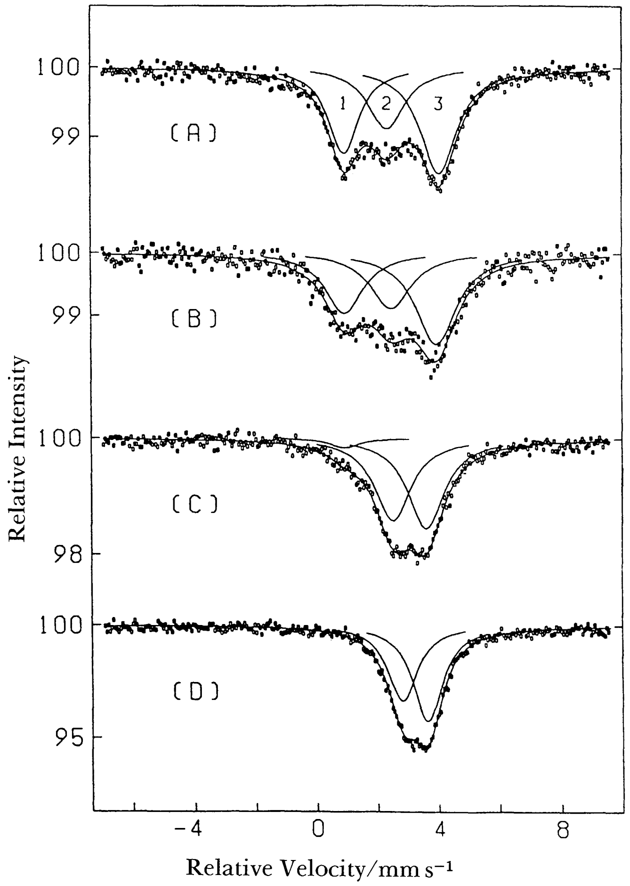

Fig. 3. Mössbauer emission spectra of $^{119m}Te \rightarrow {}^{119}Sb \rightarrow {}^{119}Sn$ in α-irradiated $^{117}SnSe$ (measurement at liquid nitrogen temperature). (A) As irradiated, (B) after 1 h annealing at 100 °C, (C) after 1 h annealing at 200 °C, and (D) after 1 h annealing at 600 °C.

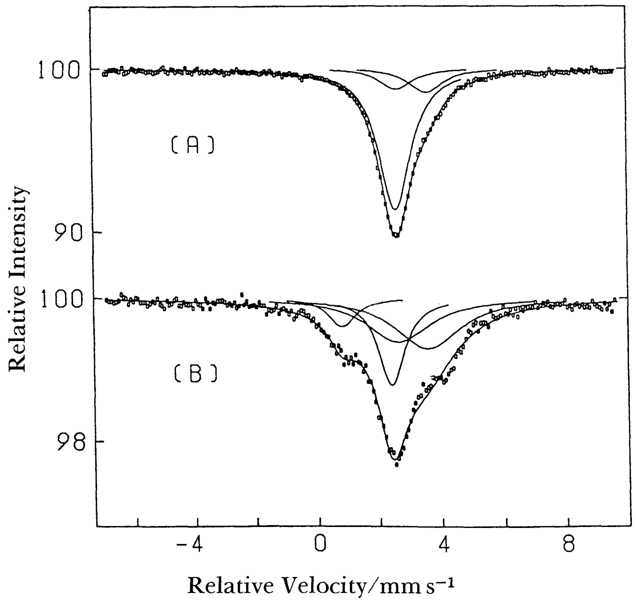

Fig. 4. Mössbauer emission spectra of SnS samples fused and recrystallized with additional 3 at. % ^{120}Sn or ^{117}Sn metal after p- or α-irradiation (measurement at liquid nitrogen temperature). (A) $^{120}Sn_{1.03}S(^{119}Sb)$, (B) $^{117}Sn_{1.03}S(^{119m}Te)$.

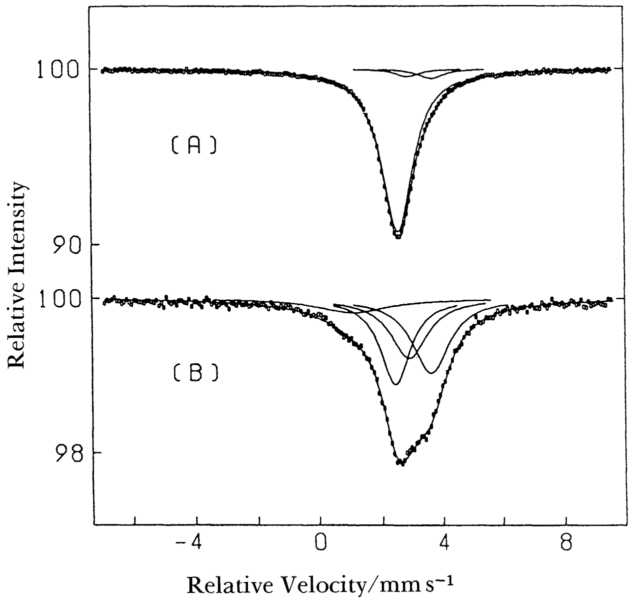

Fig. 5. Mössbauer emission spectra of SnSe samples fused and recrystallized with additional 3 at. % ^{120}Sn or ^{117}Sn metal after p- or α-irradiation (measurement at liquid nitrogen temperature). (A) $^{120}Sn_{1.03}Se(^{119}Sb)$, (B) $^{117}Sn_{1.03}Se(^{119m}Te)$.

centers and widths remaining almost unchanged.

The emission spectra of stoichiometric ^{117}SnS and $^{117}SnSe$ samples fused and recrystallized after α-irradiation gave spectra similar to those of p-irradiated samples. Figure 4 shows the spectra of ^{120}SnS and ^{117}SnS fused and recrystallized with an additional 3 at. % ^{120}Sn or ^{117}Sn metal after p- or α-irradiation. The samples are designated as $^{120}Sn_{1.03}S(^{119}Sb)$ and $^{117}Sn_{1.03}S(^{119m}Te)$, though their X-ray patterns show that they are not single phase and contain a small amount of β-Sn. The spectra of similarly obtained $^{120}Sn_{1.03}Se(^{119}Sb)$ and $^{117}Sn_{1.03}Se(^{119m}Te)$ are shown in Fig. 5.

Discussion

Both SnS and SnSe have a rhombically distorted NaCl-type crystal structure ($Pnma$-D_{2h}^{16}). The nuclear reactions and decay sequences studied in this work are:

$$^{120}Sn(p,2n)^{119}Sb \xrightarrow{EC} {}^{119}Sn^{*} \longrightarrow {}^{119}Sn$$

and

$$^{117}Sn(\alpha,2n)^{119m}Te \xrightarrow{EC} {}^{119}Sb \xrightarrow{EC} {}^{119}Sn^{*} \longrightarrow {}^{119}Sn.$$

Here, $^{119}Sn^{*}$ signifies ^{119}Sn in the nuclear first excited state (Mössbauer level).

The p- and α-reactions impart the ^{119}Sb and ^{119m}Te atoms with a recoil energy that is sufficient for their displacement from the sites of the target atoms. In the following EC decay of ^{119m}Te to ^{119}Sb, the neutrino emitted from the nucleus imparts on the atom a recoil energy amounting to 24 eV. The γ-quanta emitted in cascades give recoil energies up to a maximum value of 20 eV. Assuming that these particles are emitted isotropically, the total recoil energy is estimated to have a distribution with a minimum below the displacement energy, E_d (roughly 25 eV for metals[14] and somewhat smaller for compounds), and a maximum exceeding it. Therefore, a part of the ^{119}Sb atoms are expected to be displaced from the site of ^{119m}Te as a result of the decay; the others remain in the original site of ^{119m}Te. This was experimentally demonstrated in our previous study on Sn^{119m}Te and $Sb_2{}^{119m}Te_3$ samples.[11] On the other hand, the recoil energy of the EC decay of ^{119}Sb is estimated to be 1.5 eV. Since it is smaller than the displacement energy in a solid, the ^{119}Sn atoms arising from ^{119}Sb remain in the position of the ^{119}Sb atoms after the decay.

We attribute the doublets observed for *p*-irradiated ^{120}SnS and ^{120}SnSe (Figs. 1(A) and (B)) to ^{119}Sn at normal Sn sites of the matrices on the basis of the similarity of their Mössbauer parameters to those of normal tin atoms in SnS and SnSe observed by conventional Mössbauer absorption measurements on the compounds.[15,16] It is concluded from the observation that the energetic ^{119}Sb atoms produced by the proton reaction are exclusively stabilized at the scarcely perturbed Sn sites of SnS and SnSe, since the recoil energy of the EC decay of ^{119}Sb is smaller than the displacement energy in solid, as described above. Namely, in the last stage of recoil the ^{119}Sb atoms replace an Sn atom in the matrix and the Sn atom is displaced to a position at which the resulting defect structure does not affect the Mössbauer parameters of ^{119}Sn arising from ^{119}Sb. This forms a contrast to the case of ^{120}SnTe, in which ^{119}Sb atoms occupy both the Sn and Te sites after the *p*-reaction.

The results on α-irradiated samples show that the effect of the α-reaction and the EC decay is entirely different from that of the *p*-reaction. Lines 1—3 observed for α-irradiated ^{117}SnS and ^{117}SnSe (Figs. 2(A) and 3(A)) can be hardly assigned to known chemical species of Sn having S or Se ligands. On the basis of the isomer shift, Line 1 is assigned to $^{119}Sn^{4+}$ ions accompanied by a nearby defect. The behavior of Lines 2 and 3 upon annealing suggests that they are correlated. After 1 h of annealing at 600 °C, the lines turned out to be a quadrupole doublet assignable to ^{119}Sn at the normal Sn site of SnS or SnSe (Figs. 2(D) and 3(D)). Therefore, Lines 2 and 3 in Figs. 2(A) and 3(A) are ascribed to a quadrupole doublet of ^{119}Sn at Sn site of SnS or SnSe accompanied by a certain defect. Since the isomer shift is virtually the same as that of normal tin atoms in SnS or SnSe, the number of sulfide or selenide ions in the first coordination sphere is not considered to be different from that of normal Sn in SnS or SnSe. The distortion in the first coordination sphere or the defect in the second or further coordination sphere is most probable.

It is to be noted here that the effects of annealing were observed not on ^{119}Sb, but on ^{119m}Te in the experiment described above, since the annealed samples were measured after the ^{119}Sb subjected to annealing had decayed and a radioactive equilibrium between ^{119m}Te and ^{119}Sb had been attained. As described above, the ^{117}SnS and ^{117}SnSe samples fused and recrystallized after irradiation showed no trace of defect structures. Those with chemically doped ^{119m}Te also gave similar results. It is evident from these observations that the defect structures are not the result of the EC decay of ^{119m}Te, but of the α-reaction.

In the thoroughly annealed, fused, and chemically doped samples ^{119m}Te are considered to be at the S or Se site on the basis of a similarity in the chemical properties of the elements. A part of ^{119}Sb atoms arising from ^{119m}Te are displaced from the site due to recoil associated with EC decay. For the rest of ^{119}Sb, although the recoil energy is insufficient for any displacement, the S or Se site is much less favorable for ^{119}Sb than the Sn site with regard to its chemical nature. Namely, the physical and chemical properties of Sb are much closer to that of Sn than to S or Se. Consequently, all of the ^{119}Sb atoms are stabilized at only the Sn site. On the other hand, the properties of Sb lie just in the middle of those of the components of the matrix in the case of SnTe. This enables stabilization of Sb in both sites.

Computer simulations on metal showed that a recoil atom of the same element as the matrix most frequently replaces a lattice atom in the final stage of its energy dissipation and are stabilized at the substitutional site.[17—19] On the other hand, it has been shown that implanted iron atoms tend to occupy interstitial sites in metals having large atomic volumes.[2] In case of ^{119}Sb after the *p*-reaction, the recoil atom is considered to replace mainly a ^{120}Sn atom, which has a mass close to that of ^{119}Sb and rests at the site. Moreover, the experimental results described above show that the ^{119}Sb atoms stopped at the S or Se site or at an interstitial site move to an Sn site which is chemically much more favorable for them than the S or Se site.

From only a kinematical point of view, the ^{119m}Te recoil atoms are considered to dominantly replace ^{117}Sn in the SnS or SnSe matrix. However, the Sn site is not favorable for ^{119m}Te and a certain metastable defect structure including the surrounding S or Se atoms are formed. This structure is considered to be partly preserved, even after the decay of ^{119m}Te, and to be reflected in the spectra of α-irradiated ^{117}SnS and ^{117}SnSe before annealing (Figs. 2(A) and 3(A)).

Measurements on the SnS and SnSe samples fused and recrystallized with 3 at. % Sn metal were undertaken in order to determine whether stabilization of diluted ^{119}Sb at the S and Se sites is not allowed at all in SnS and SnSe. The SnS or SnSe phase in the samples is considered to be saturated with Sn. This is considered to be a condition promoting ^{119}Sb to the S or Se site based on the result on SnTe.[12] Besides the doublet of SnS or SnSe, a dominant line with an isomer shift of 2.56±0.03 mm s^{-1} was found in the spectra of ^{120}Sn$_{1.03}$S(^{119}Sb) and ^{120}Sn$_{1.03}$Se(^{119}Sb) samples (Figs. 4(A) and 5(A)). Since the isomer shift is in good agreement with that of β-Sn,[20] this line is assigned to ^{119}Sn arising from ^{119}Sb dissolved in the β-Sn phase of the samples. The large relative intensity of the line shows that ^{119}Sb is much more soluble in β-Sn than in SnS or SnSe. In the ^{117}Sn$_{1.03}$S(^{119m}Te) and ^{117}Sn$_{1.03}$Se(^{119m}Te) samples (Figs. 4(B) and 5(B)), the relative intensity of the peak due to β-Sn is much smaller than in ^{120}Sn$_{1.03}$S(^{119}Sb) and ^{120}Sn$_{1.03}$Se(^{119}Sb). The origin of this large difference is ascribed to the higher solubility of ^{119m}Te, than that of ^{119}Sb, in SnS and SnSe which have a homologous element of Te as a component. The lines with isomer shifts of 0.82 and 1.07 observed for the ^{117}Sn$_{1.03}$S(^{119m}Te) and ^{117}Sn$_{1.03}$Se(^{119m}Te) samples are attributed to the Sn^{4+} species, the origin of which is not understood. They may be the same species as those observed in α-irradiated ^{117}SnS and ^{117}SnSe. In any case, we conclude that no line ascribable to ^{119}Sn at S or Se site of the matrices has been identified in the specta of samples fused with excess Sn metal,although the possibility is not denied that one is hidden in the large peak due to ^{119}Sb in β-Sn.

The authors are thankful to the staff of the RIKEN 160 cm cyclotron for many irradiation runs and also to Mr. Y. Iimura for X-ray powder pattern measurements.

References

1) G. Weyer, *Hyperfine Interact.*, **27**, 249 (1986).

2) M. Menningen, R. Sielemann, G. Vogl, Y. Yoshida, K. Bonde-Nielsen, and G. Weyer, *Hyperfine Interact.*, **35**, 807 (1987).

3) G. Weyer, *Hyperfine Interact.*, **43**, 187 (1988).

4) J. A. Sawicki and B. D. Sawicka, *Nucl. Instrum. Methods, Phys. Res., Sect. B*, **46**, 38 (1990).

5) S. Laubach, P. Schwalbach, M. Hartick, E. Kankeleit, B. Keck, and R. Sielemann, *Hyperfine Interact.*, **53**, 75 (1990).

6) H. Bemelmans, G. Borghs, and G. Langouche, *Hyperfine Interact.*, **56**, 1553 (1990).

7) H. Binczycka, G. Marest, N. Moncoffre, and J. Stanek, *Hyperfine Interact.*, **56**, 1557 (1990).

8) D. Mo, G. L. Zhang, Z. N. Liang, and L. Niesen, *Hyperfine Interact.*, **56**, 1621 (1990).

9) G. L. Zhang, D. Mo, Z. N. Liang, and L. Niesen, *Hyperfine Interact.*, **56**, 1661 (1990).

10) P. Zhang, L. Urhahn, I. Dězsi, A. Vantomme, and G. Langouche, *Hyperfine Interact.*, **56**, 1667 (1990).

11) F. Ambe and S. Ambe, *J. Chem. Phys.*, **73**, 2029 (1980).

12) F. Ambe and S. Ambe, *J. Chem. Phys.*, **75**, 2463 (1981).

13) Partly presented at the Intern. Conf. on the Appl. of the Mössbauer Effect, Crayton, 1987.

14) F. Seitz, in "Solid State Physics," ed by F. Seitz and D. Turnbull, Academic, New York (1956), Vol. 2, p. 305.

15) J. D. Donaldson and B. J. Senior, *J. Inorg. Nucl. Chem.*, **31**, 881 (1969).

16) V. Fano and I. Ortalli, *J. Chem. Phys.*, **61**, 5017 (1974).

17) J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, *Phys. Rev.*, **120**, 1229 (1960).

18) C. Erginsoy, G. H. Vineyard, and A. Englert, *Phys. Rev. A*, **133**, 595 (1964).

19) C. Erginsoy, G. H. Vineyard, and A. Shimizu, *Phys. Rev, A*, **139**, 118 (1965).

20) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy," Chapman and Hall, London (1971), p. 374.