

A site distribution study of dilute ^{119}Sb and $^{119\text{m}}\text{Te}$ on solidification of SnTe and SnSb by Mössbauer emission spectroscopy of ^{119}Sn

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Citation: *The Journal of Chemical Physics* **75**, 2463 (1981); doi: 10.1063/1.442270

View online: <http://dx.doi.org/10.1063/1.442270>

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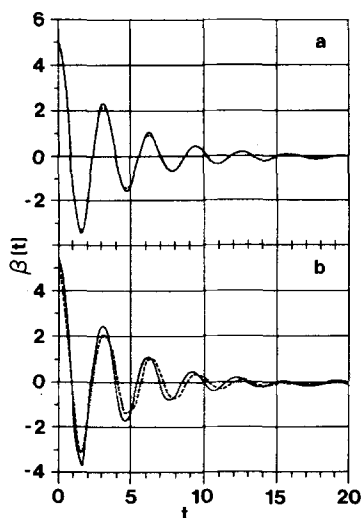


FIG. 1. Calculated (—) and true (---) values of the memory kernel $\beta(t)$ for different time intervals t_0 . (a) $t_0 = 0.2$, (b) $t_0 = 0.4$.

increasing the sampling frequency.

The procedure described here, like the interpolation procedure,³ has an advantage over curve fitting in that no prior assumptions concerning the form of $\beta(t)$ are required. The kernel $\beta(t)$ could also be extracted from Eq. (4) by a Fourier transform method, but the relatively poor accuracy of the time correlation functions at long

times would then be reflected even in the short time values of $\beta(t)$. In the present method, as in Ref. 3, short time values of $\beta(t)$ are determined from short time values of the correlation functions. The present method is much simpler to implement than the interpolation procedure, but does require initial calculation of two ($\Omega = 0$) or three correlation functions instead of just one. As it stands, the method will readily yield accurate representations of $\beta(t)$ for a wide variety of time correlation functions.

This work was supported in part by the National Science Foundation. J.A.M. is an Alfred P. Sloan Fellow and the recipient of an N.I.H. Research Career Development Award.

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NOTES

A site distribution study of dilute ^{119}Sb and ^{119m}Te on solidification of SnTe and SnSb by Mössbauer emission spectroscopy of ^{119}Sn

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(Received 24 March 1981; accepted 14 May 1981)

Distribution of dilute impurity atoms among different phases on crystallization of a melt can be easily followed with the aid of a carrier-free radioactive tracer. However, information on their distribution among different lattice positions in a phase is not so readily accessible, unless they exhibit spectroscopic characteristics specific to each site and observable with high sensitivity. This paper reports that combination of the radioactive tracer technique and Mössbauer emission spectroscopy provides a useful method for studying the behavior of dilute impurity atoms on solidification of molten binary systems with experimental examples of 38.0 h ^{119}Sb and 4.68 d ^{119m}Te in SnTe and SnSb .

The phase diagram of the ternary system Sn-Sb-Te was extensively studied by Stegherr.¹ It is seen from the diagram that SnTe and SnSb can dissolve a small amount of Sb and Te , respectively, retaining their NaCl -type structure. No information is, however, available yet on the distribution of the dissolved Sb and Te impurity atoms among different lattice positions in the phases.

Recently, we reported the Mössbauer parameters of defect ^{119}Sn atoms occupying the Te site of SnTe and the Sb site of SnSb .² This made possible, together with the results of conventional absorption measurements, dis-

crimination of the Sn atoms in the cationic and anionic sites of the matrices by Mössbauer spectroscopy. As the EC decay of ^{119}Sb to ^{119}Sn brings about no atomic displacement in solid,^{2,3} distribution of ^{119}Sb between the two lattice sites of SnTe is thus directly determined from the emission spectra of the daughter ^{119}Sn . The lattice position of ^{119m}Te is not necessarily the same as that of its granddaughter nuclide ^{119}Sn , since the possibility of atomic displacement by recoil is not ruled out in the first step of the EC decay series $^{119m}\text{Te} \rightarrow ^{119}\text{Sb} \rightarrow ^{119}\text{Sn}$. However, the distribution of ^{119m}Te in SnSb can be deduced from the emission spectrum of ^{119}Sn by considering the spectrum of the recoil energy associated with the EC decay.^{2,3}

Stoichiometric $^{120}\text{SnTe}$ was irradiated with 16 MeV protons to produce carrier-free ^{119}Sb directly in the matrix by the $^{120}\text{Sn}(p, 2n)^{119}\text{Sb}$ reaction. The details of target preparation and irradiation were described in a previous paper.² The irradiated $^{120}\text{SnTe}$ was fused and recrystallized in a vycor tube under Ar. In case of nonstoichiometric samples appropriate amount of ^{120}Sn or Te metal was added before fusion. $^{117}\text{SnSb}$ samples containing carrier-free ^{119m}Te were obtained similarly utilizing the $^{117}\text{Sn}(\alpha, 2n)^{119m}\text{Te}$ reaction.

Mössbauer emission spectra of ^{119}Sn arising from ^{119}Sb in the sources were measured at 78 K as described in Ref. 2. The obtained spectra were least-squares fitted to Lorentzians on FACOM 230-75 computer of the Institute.

In the Sn-Te binary system, the region of stability for the solid SnTe phase is known to exist only on the Te-rich side and excess Te is counterbalanced by cation vacancies.^{4,5} Mössbauer emission measurements were performed on sources obtained by crystallizing Sn-Te melts with the atomic ratios of 1:0.97, 1:1, and 1:1.03 containing carrier-free ^{119}Sb . The SnTe and $\text{SnTe}_{1.03}$ samples lying approximately at both ends of the stability region were of single phase within the detection limit of our powder x-ray pattern measurement. In the $\text{SnTe}_{0.97}$ source segregation of excess Sn as β tin was observed.

The Mössbauer emission spectra of ^{119}Sb in the SnTe sources at 78 K are shown in Fig. 1. As seen in Fig. 1(b), the SnTe(^{119}Sb) sample prepared by crystallization of a stoichiometric melt gave two emission lines with the isomer shifts of 2.36 ± 0.05 and 3.3 ± 0.1 mm/s relative to BaSnO_3 at 78 K. The lines are attributed to ^{119}Sn occupying the Te and Sn sites of SnTe, respectively, since their isomer shifts are in good agreement with the reported values for ^{119}Sn in the two lattice sites.² In repeated measurements the relative area of the two peaks showed a certain fluctuation probably due to slight deviation of the composition from the stoichiometry (estimated to be of the order of 0.3%). The rate of cooling of the melts (slow cooling or quenching) gave no significant effect on the relative area. In every case no third peak assignable to interstitials or aggregates was observed.

The spectra of samples obtained from nonstoichiometric melts are given in Figs. 1(a) and 1(c). The emission spectrum of the source crystallized from a melt

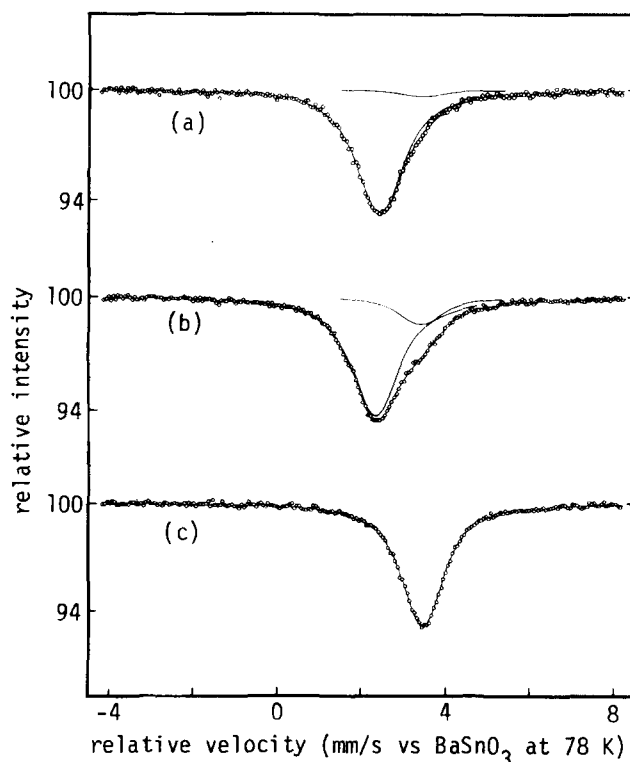


FIG. 1. Mössbauer emission spectra of ^{119}Sn arising from carrier-free ^{119}Sb in the (a) $\text{SnTe}_{0.97}$, (b) SnTe, and (c) $\text{SnTe}_{1.03}$ samples crystallized from melts.

containing excess tin, $\text{SnTe}_{0.97}$ (^{119}Sb), was composed of a dominant line with an isomer shift corresponding to ^{119}Sn in the Te site and a minute shoulder assignable to ^{119}Sn occupying the Sn site [Fig. 1(a)]. On the other hand, the Te-excess sample, $\text{SnTe}_{1.03}$ (^{119}Sb), gave only one emission line corresponding to ^{119}Sn in the Sn site [Fig. 1(c)].

Since ^{119}Sn remains in the same lattice site as the parent nuclide ^{119}Sb in the EC decay, the position of ^{119}Sb before the decay is the same as that of ^{119}Sn determined from the emission spectra. Therefore, the observations on the SnTe samples lead to the conclusion that carrier-free ^{119}Sb was distributed between the Sn and Te sites of SnTe on crystallization, and that the distribution was strongly dependent on the composition of the matrices. In other words, ^{119}Sb can replace both the Sn and Te atoms in SnTe to form cationic and anionic point defects respectively. It is also seen from the results on nonstoichiometric samples that ^{119}Sb atoms are incorporated preferentially into the anionic site of SnTe when the phase is saturated with cations ($\text{SnTe}_{0.97}$), but that they are stabilized exclusively in the cationic site when the matrix is deficient in cations ($\text{SnTe}_{1.03}$).

The SnSb sample prepared by crystallizing a melt containing carrier-free ^{119m}Te gave a single emission line with an isomer shift of 2.37 ± 0.05 mm/s. The spectrum is essentially the same as that of the labeled source Sn ^{119}Sb ,² which indicates that all the ^{119}Sb atoms arising from ^{119m}Te in the SnSb(^{119m}Te) source were in the Sb site.

In the recoil energy spectrum of the $^{119m}\text{Te} \xrightarrow{\text{EC}} ^{119}\text{Sb}$ decay the lower part thereof is estimated to be small enough to retain the decaying atom in the original lattice site.^{2,3} This has been experimentally verified for the sources $\text{Sn } ^{119m}\text{Te}$ and $\text{Sb}_2 ^{119m}\text{Te}_3$, in which the majority of ^{119}Sb was found in the Te site.² Therefore, an appreciable amount of ^{119}Sb should have been found remaining in Sn site of the $\text{SnSb}(^{119m}\text{Te})$ sample, if a part of ^{119m}Te had been distributed in the Sn site on crystallization. Accordingly, it is concluded from the exclusive distribution of ^{119}Sb in Sb site of the sample that no ^{119m}Te was stabilized in the Sn site on crystallization of the SnSb melt.

The observations above on the distribution of ^{119}Sb in SnTe and ^{119m}Te in SnSb can be interpreted in a unified manner considering the electronegativity of the three elements involved. Dilute Sb atoms can take part in the formation of SnTe lattice from a melt as both cationic and anionic point defects occupying the Sn and Te sites, supplying preferentially the deficient constituent in case of nonstoichiometric samples, because they have an

electronegativity value lying between those of Sn and Te. On the other hand, Te is exclusively incorporated into the anionic site of SnSb , since it is even more electronegative than the anionic component of the matrix.

The present work shows that Mössbauer emission spectroscopy is a useful method for the site-distribution study of dilute atoms in binary compounds. It would be interesting to apply this technique to other systems in order to study how electronegativity competes with other factors in determining the distribution of dilute impurity atoms in solids.

We wish to thank the staff of IPCR cyclotron for p - and α -irradiations.

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Resonance state lifetimes from stabilization graphs

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(Received 20 January 1981; accepted 18 May 1981)

The stabilization method (SM) pioneered by Taylor and co-workers¹ has proven to be a valuable tool for estimating the energies of long-lived metastable states of electron-atom, electron-molecule, and atom-diatom complexes. In implementing the SM one searches for eigenvalues arising from a matrix representation of the relevant Hamiltonian H which are "stable" as the basis set used to construct H is varied.

To obtain lifetimes of metastable states, one can choose from among a variety of techniques²⁻⁷ (e.g., phase shift analysis, Feshbach projection "golden rule" formulas, Siegert methods, and complex coordinate scaling methods), many of which use the stabilized *eigenvector* as starting information. Here we demonstrate that one can obtain an *estimate* of the desired lifetime directly from the stabilization graph in a manner which makes a close connection with the complex coordinate rotation method (CRM) for which a satisfactory mathematical basis exists.

The starting point of our development is the observation that both the stable eigenvalue (E_s) and the eigenvalue(s) (E_c) which come from above and cross E_s (see Fig. 1 and Refs. 9-11 and 13) vary in a nearly linear manner (with α) near their avoided crossing points. This observation leads us to propose that the two eigenvalues arising in each such avoided crossing can be

thought of as arising from two "uncoupled" states having energies $\epsilon_s(\alpha) = \epsilon + S_s(\alpha - \alpha_c)$ and $\epsilon_c(\alpha) = \epsilon + S_c(\alpha - \alpha_c)$, where S_s and S_c are the slopes of the linear parts of the stable and "continuum" eigenvalues, respectively. α_c is the value of α at which these two straight lines would intersect, and ϵ is their common value at $\alpha = \alpha_c$. This modeling of ϵ_s and ϵ_c is simply based upon the *observa-*

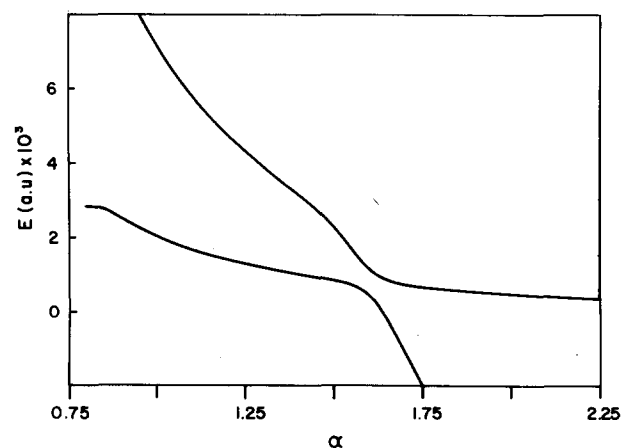


FIG. 1. Stabilization graph for the 2π shape resonance state of LiH^- (Ref. 9).