

Studies of small Fe-Sn clusters in an argon matrix

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The Mössbauer effect in ^{119}Sn and ^{57}Fe was employed to study and characterize small clusters of Fe_xSn_y formed and stabilized in a solid argon matrix. Various low concentrations of Fe and Sn atoms in Ar were used (0.1–0.5 at. %), resulting in formation of dimers and trimers. The constituents and geometrical structures were confirmed by self-consistent assignment of the ^{57}Fe isomer shift, quadrupole splitting, linewidth, and relative intensities of the ^{57}Fe and ^{119}Sn lines. Apart from the monomers and dimers of Fe and Sn, the following species were characterized: FeSn , Fe_2Sn , FeSn_2 , SnFeSn , and Fe_3 . Conclusions were drawn regarding the reactivity of Fe and Sn atoms and dimers in the matrix preceding solidification of argon. The nature of the Fe–Sn bond is discussed in terms of the ^{57}Fe hyperfine constants.

INTRODUCTION

The formation and characterization of small metal clusters composed of only a few atoms were the subject of several studies in recent years.¹ The main objective was to elucidate several aspects of the small clusters in terms of geometrical structure and electronic or valence configuration. The knowledge gained from this information might have an important role concerning the nature of the solubility of different atoms to form alloys, the understanding of crystallographic structure, and the engineering of small clusters for industrial applications.

A widely used method for formation of such small clusters is by direct reaction of individual atoms or molecules in a solid rare-gas matrix at low temperature. The matrix is used as a medium for both formation and stabilization, and *in situ* studies of the clusters. Normally, a distribution of cluster sizes is obtained, depending among other factors, on the metal-to-gas ratio, type of matrix gas, temperature of substrate, etc. The main technique employed to identify and characterize the small clusters is optical spectroscopy in its whole range, from uv to far infrared and Raman.² However, owing to spectral overlap resulting from the presence of several clusters in the matrix, interpretation in cases of wide distribution of sizes is sometimes dubious.

Following the successful application of the

Mössbauer effect (ME) in studies of single atoms and molecules in rare-gas matrices,³ and in ^{57}Fe heteronuclear diatomics,⁴ this technique has emerged as a promising tool for the investigation of small clusters. A single measurement displays a set of data, which when combined, provides self-consistent information resulting in more reliable characterization of the small clusters. Among the most important information is the following: (a) *relative abundance* of the individual clusters via the absorption peak intensities, (b) *geometrical structure* via the quadrupole coupling constants (ΔE_Q), and (c) *electronic configuration* of the Mössbauer atom ground state via the isomer shift (IS).

The present studies were motivated by the possible applications of two γ -resonance probes in a single sample of clusters. ME studies, as will be shown, were performed both on ^{57}Fe and ^{119}Sn in Fe_xSn_y clusters, formed and trapped in solid argon. The experimental details concerning the specially built system will be described, and the discussion will be devoted to the diagnostics, reactivity of Fe-Sn atoms, and implications of the hyperfine-interaction constants to the nature of the Fe–Sn chemical bond.

EXPERIMENTAL

The samples were produced and measured in a system specially designed for ME matrix-isolation experiments. The present system differs from oth-

er ME systems³ employing techniques adapted from optical matrix isolation,² in the sense that it was designed for efficient ME studies. Two details were particularly emphasized, namely: (a) high evaporation yield of metal atoms, necessary for the enriched isotopes of ⁵⁷Fe and ¹¹⁹Sn, and (b) optimum geometry for high γ -ray counting.

The system consists of a commercial evaporator, a custom-made stainless-steel collar comprising several windows and oven entrances, and a top-mounted cryostat. The cryostat can be rotated to allow for perfect alignment both for the matrix deposition and for the ME experiments. A cross section of the system is shown in Fig. 1. The substrate consisted of an iron-free Be disk thermally anchored to a copper tail, isolated from the main He bath. Cooling was achieved by passing liquid helium through a copper-tube coil surrounding the copper tail, assisted by a vacuum pump.

The rate of deposition of the individual Fe and Sn atom beams was monitored with precalibrated quartz crystals attached to the outer radiation shield (see Fig. 1). Typical deposition rates of metals and Ar were 5×10^{-9} and 4×10^{-6} mol/cm² min, respectively. During evaporation, the temperature measured near the Be disk was 7 ± 1 K and measurements were performed at $T = 4.5$ K. A 50-mCi Rh (⁵⁷Co) source and a 10-mCi CaSnO₃

source were used for Fe and Sn measurements, respectively.

Many spectra were recorded, having different Fe-to-Sn and metal-to-gas ratio. In general it was found that in order to avoid the growing of large clusters it was necessary to operate under conditions where the metal concentration was considerably lower than 1 at. %, and the substrate temperatures were below 8 K. The last condition was not always easy to achieve because of the proximity of the ovens to the matrix. This relatively short distance resulted in warming up of the outer argon layers; thus, even at metal concentrations of 0.1 at. %, metal clusters were formed in contradiction to statistical predictions⁵ of the formation of mainly monomers. The only spectra considered were those where both monomers and dimers were present with relatively large proportions.

In Figs. 2(a) and 2(b), the absorption spectra of ⁵⁷Fe and ¹¹⁹Sn, respectively, are depicted for the cases of three different Fe-to-Sn and metal-to-gas ratios. In the case of Sn, only three components could be reliably analyzed, namely the Sn⁰ monomer, Sn₂ dimer, and a convolution of spectra due to Fe_xSn_y clusters. The poor resolution of the convoluted spectrum can be attributed to, not only the intrinsic resolution of ¹¹⁹Sn resonance, but also to the possible similar values of the hyperfine constants of the ¹¹⁹Sn-Fe clusters. This was not the case, for instance, in ¹¹⁹Sn-Cu and ¹¹⁹Sn-Ag clusters⁶ where several spectral components could be identified.

The ⁵⁷Fe spectra were well resolved. The high quality of the spectra allowed us to characterize with a high degree of reliability several Fe_xSn_y species. In Table I, the results obtained from the least-squares-fitting are presented. The complexity of the spectra imposed several restrictions on the fitting, such as the requirement of consistent evolution of clusters with concentration and plausible hyperfine interaction constants. The positions of the Fe⁰, Fe₂, and Fe₃ lines, known from pure-iron experiments, were fixed and all other components were restricted to having quadrupole split doublets. The accepted fittings were those that could accommodate identical values of ΔE_Q and IS for the various concentrations.

DISCUSSION

Cluster diagnostics

The clusters were characterized by their hyperfine interaction values and the relative intensities

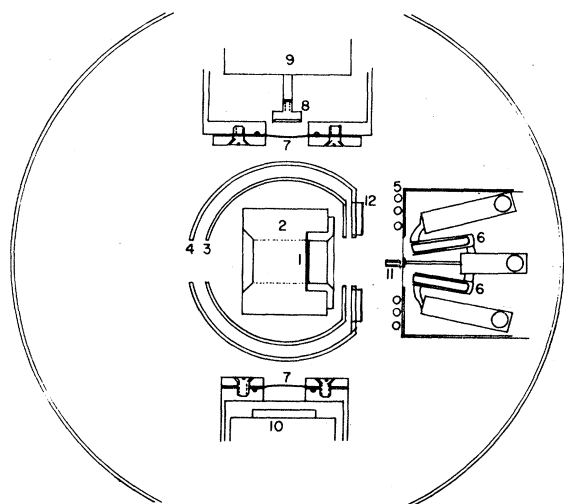


FIG. 1. The cross section of the Mössbauer matrix isolation system: 1—Be substrate, 2—Cu block, 3 and 4—radiation shields, 5—water-cooled radiation shield of evaporation ovens, 6—evaporation ovens for Fe and Sn, 7—Mylar windows, 8—Mössbauer source, 9—Doppler-shift driver, 10—radiation detector, 11—argon entrance, and 12—quartz crystals attached to the liquid-nitrogen radiation shields.

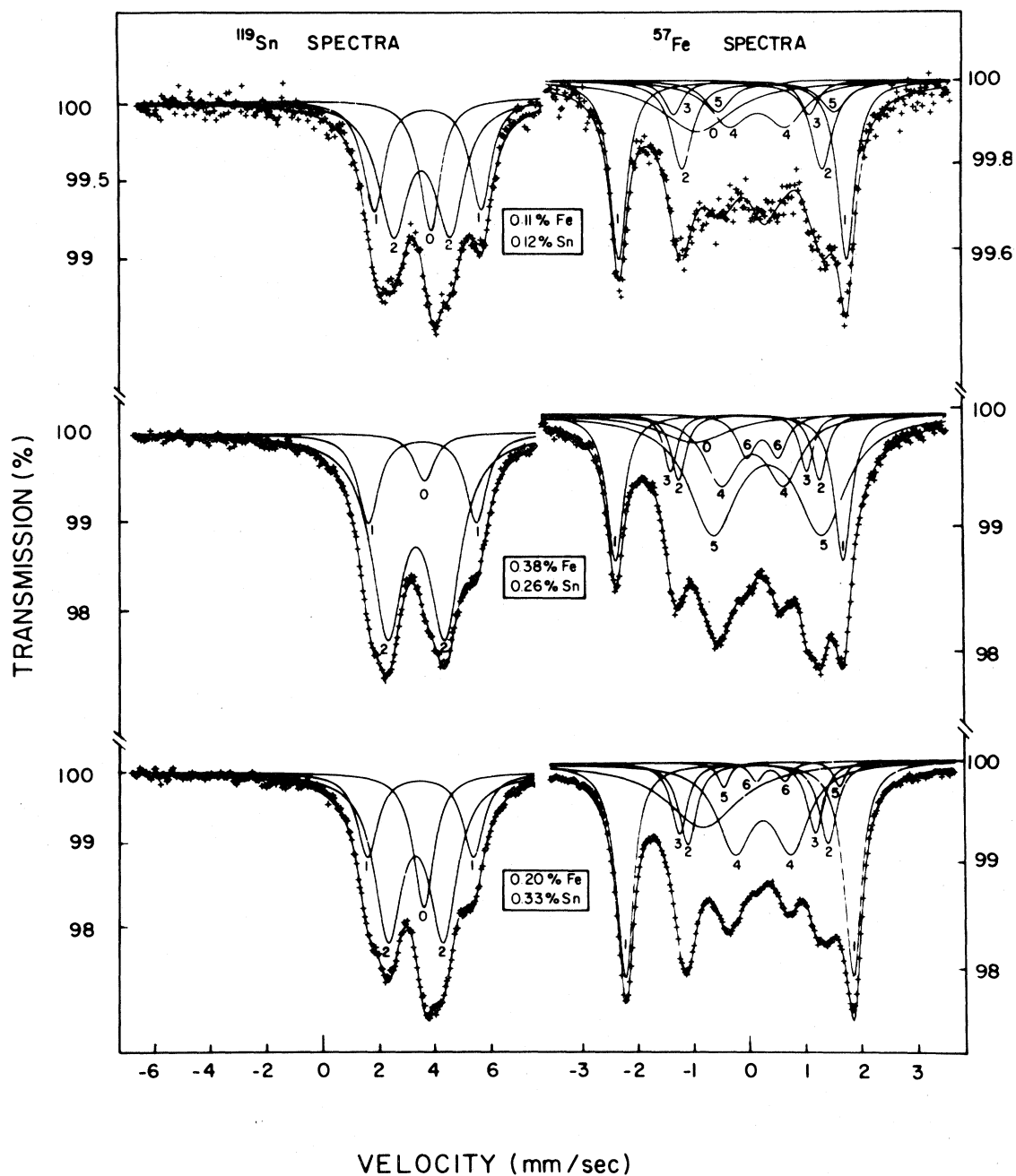


FIG. 2. ^{57}Fe and ^{119}Sn absorption spectra for various metal-to-gas ratios. The solid line is a least-squares fit of the experimental spectra. Six and three components were characterized for ^{57}Fe and ^{119}Sn spectra, respectively.

of their absorption peaks. The quadrupole splitting values are a measure of the geometrical structure. The larger the quadrupole splitting, the more linear will be the Fe-Fe or Fe-Sn bonds. In the monomer-trimer series, the more positive the

values of the IS, the more iron atoms are present in the cluster.⁷ The trend of the line intensity as a function of concentration played an important role in the clusters diagnostics. For thin absorbers, the intensity I of an individual component, as given by

TABLE I. Experimental and calculated values of the various clusters. IS is the Fe and Sn isomer shift with respect to iron metal and CaSnO_3 , respectively, ΔE_Q is the quadrupole splitting, Γ is the experimental linewidth, f is the recoil-free fraction (see text), I is the normalized relative area, c is the calculated abundance of clusters (see text).

Component	Assignment	IS (mm/sec)	ΔE_Q (mm/sec)	Γ (mm/sec)	f	Fe=0.11 at. %		Fe=0.38 at. %		Fe=0.20 at. %	
						Sn=0.12 at. %	c (%)	Sn=0.26 at. %	c (%)	Sn=0.33 at. %	c (%)
						I (%)	c (%)	I (%)	c (%)	I (%)	c (%)
^{57}Fe	0	Fe^0	-0.78(2)	0	0.60	19(2)	30(3)	7(1)	15(3)	20(2)	13(2)
	1	Fe_2	-0.154(2)	4.07(1)	0.76	31(3)	19(2)	18(2)	14(2)	30(2)	19(2)
	2	FeSn	0.20(1)	2.52(2)	0.84	19(2)	21(2)	7(1)	10(1)	13(1)	14(1)
	3	$\text{Fe}(\text{Sn}_2)$	0.09(2)	2.42(2)	0.90	16(1)	7(1)	6(1)	8(1)	9(2)	9(2)
	4	SnFeSn	0.28(2)	1.05(3)	0.90	16(2)	17(2)	17(2)	23(2)	24(3)	24(3)
	5	Fe_2Sn	0.57(3)	2.01(1)	0.87	8.5(1)	5(1)	39(3)	27(3)	2.0(1)	10(5)
	6	Fe_3	0.44(2)	0.54(2)	0.84	<0.5(3)	<0.1(1)	5(1)	3(1)	2.0(1)	10(5)
^{119}Sn	0	Sn^0	3.18(2)	0	0.5	18(2)	35(2)	6(1)	13(2)	17(2)	33(3)
	1	Sn_2	3.05(3)	3.77(2)	0.7	31(2)	21(2)	22(3)	17(3)	21(3)	14(2)
	3	Sn_xFe_y	2.85(1)	1.96(3)	0.75	50(3)	43(3)	72(4)	70(4)	62(3)	53(3)

the measured area, is proportional to the product of the relative abundance of a certain cluster c , the number of iron atoms in the cluster n , and the recoil-free fraction f . At low temperature f is expressed as

$$f = \exp(-3R/2k\Theta_D), \quad (1)$$

where R is the recoil energy of the whole cluster, k is the Boltzmann factor, and Θ_D is the Debye temperature of the solid argon matrix.⁸

The identification of Fe^0 and Fe_2 is straightforward and based on matrix isolation of pure iron. As a guide to the evolution of the clusters with concentration of metal atoms we refer to Fig. 3, where the intensities I of the various components (2–6) are plotted as a function of the Fe-to-Sn ratio. In Fig. 4 the values of ΔE_Q and IS of the various components are shown.

We assume that the doublet designated as 6 is the iron trimer Fe_3 . This is based on previous identification by Dyson and Montano⁷ and by our own experiment with pure iron. Component 2 is identified as FeSn . As can be seen, its intensity is the highest with equal Fe-to-Sn ratio, its ΔE_Q value is large, a consequence of a linear Fe–Sn bond, and the linewidth is narrow (see Table I) suggesting single values of ΔE_Q and IS. The intensity of component 5 is the highest in the largest value of the Fe-to-Sn ratio. This implies a cluster with Fe excess, namely a Fe_2Sn cluster. This assignment is consistent with the IS. The large value of ΔE_Q is an indication of linear Fe–Sn and/or

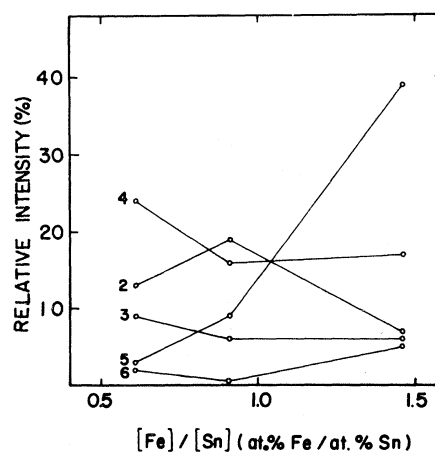


FIG. 3. Intensity trends with concentration of the various ^{57}Fe components.

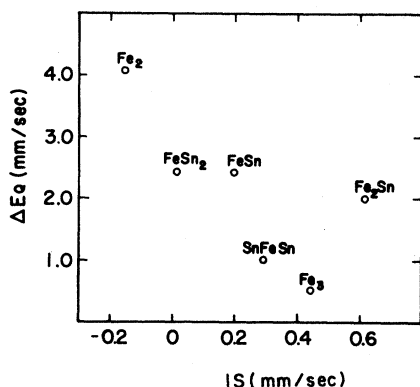


FIG. 4. Isomer shift vs quadrupole splitting of the various clusters.

Fe—Fe bonds in this cluster. Two configurations will be compatible with this assignment, namely a Fe-Sn-Fe cluster which could be linear or slightly bent or Fe-Fe-Sn having a linear structure, namely an Fe₂ dimer bound to a Sn atom. The configuration with terminal Fe will display single values of IS and quadrupole splitting (QS) and therefore narrow linewidth, whereas the configuration with two adjacent Fe atoms will reveal broad lines due to their nonidentical valence states, resulting in different values of IS and QS. The relatively broad line observed is an indication of a predominant abundance of the second type.

On similar grounds, components 3 and 4 are characterized as clusters with Sn excess, namely FeSn₂. Component 3 with a large value of ΔE_Q and narrow linewidth suggests that the iron atom is a "terminal atom," singly bound to a Sn₂ dimer. This structure could be linear or bent. Component 4 has a considerably lower ΔE_Q suggesting a bent trimer with the iron in its middle, namely Sn-Fe-Sn. The broad line of component 4 points to a distribution of Sn-Fe-Sn angle which will be reflected both in the IS and ΔE_Q values. In Fig. 5 we schematically present the possible cluster configurations as deduced from the data diagnostics of ⁵⁷Fe spectra.

The tin results are in accordance with the above mentioned assignments. In samples with low Sn concentration the occurrence of Sn⁰ is low, suggesting predominant formation of Fe₂Sn, whereas in samples with excess Sn the occurrence of Sn₂ is low due to FeSn₂ formation.

Based on the assignment of the various clusters their *f* values⁹ were calculated and are given in

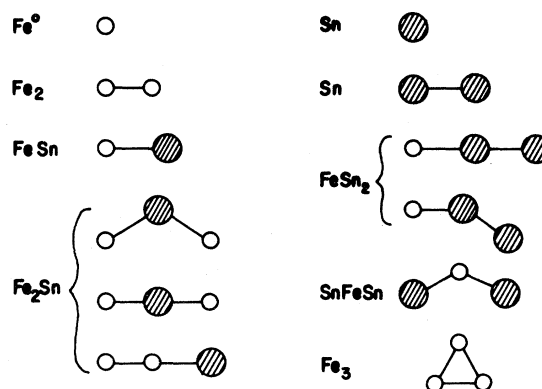


FIG. 5. Cluster structures derived from arguments based on experimental results.

Table I. Using those values, the relative concentrations (in percentage) of the clusters were obtained and are given in Table I.

The nature of the Fe—Sn bond

By examining the IS values of Fe₂, FeSn, Fe₂Sn, and Fe₃, we may draw conclusions about the nature of the Fe—Sn bond in an isolated cluster in an argon matrix. The IS value in FeSn (+0.20 mm/sec) is more positive than that of Fe₂ (−0.15 mm/sec), pointing to a considerable decrease in the *s*-electron density at the Fe nucleus. This increase could be due to any one of the following mechanisms:

- in case of pure covalent Fe—Sn bond, promotion of 4*s* electrons into the 5*d* shell,
- promotion of electrons from Sn into the *d* orbitals of Fe, or
- promotion of 4*s* electrons into the Sn orbitals.

From ME studies of FeSn alloys, Trumphy *et al.*¹⁰ concluded that electrons are promoted from Fe to Sn and deduced a value of 0.08 (4*s*) electrons per Fe—Sn bond. If this is the case in the present studies, from the difference in IS between Fe₂ and FeSn (Δ IS=0.36 mm/sec) we deduce the value of 0.2 (4*s*) electrons transferred from Fe into the Sn orbitals. The results in Fe₃ and Fe₂Sn are consistent with those of the dimers, namely the IS difference of the two trimers is 0.18 mm/sec. Thus, each Fe atom promotes approximately 0.1 (4*s*) electron to the Sn orbitals. However, the outer Fe configuration should be compatible with the quadrupole coupling constant. The value of ΔE_Q

for FeSn (equal to 2.43 mm/sec) is considerably smaller than that of a pure covalent Fe—Fe bond. The value⁸ of ΔE_q of Fe₂ is 4.05(4) mm/sec which we assume to be that of a pure $d_{3z^2-r^2}$ ground state (g.s.) configuration of Fe. A pure d_{xz} , d_{yz} state would have half its value, namely 2.02 mm/sec, which is smaller than that for FeSn. Therefore, we must assume that the Fe g.s. is not a pure $d_{3z^2-r^2}$. The reduction in the electric field gradient could be achieved by promotion of part of the 4s electrons into the d orbitals [mechanism (b)] which will be consistent with the trend in the IS and in this case will still have a pure covalent bond.

The value of ΔE_Q of ¹¹⁹Sn in the convoluted spectra of Fe_xSn_y is considerably smaller than that of Sn₂ which we assume to be due to a pure 5p state. Thus, here too, there must be a promotion of the 5s² into the 5p² orbitals which will also explain the decrease in the IS for this ¹¹⁹Sn component.

Cluster formation

From the pure aspect of probability the chances that dimers will be formed with total metal concentration of 0.2–0.5 at. % is $2-4 \times 10^{-2}$ and almost 1 for monomers. Probabilities for trimers are extremely low, of the order of 10^{-3} ; yet a large fraction of the clusters formed are dimers and trimers. Since the probability of dimers (of Sn and Fe) being emitted from the ovens is extremely small, we must conclude that chemical reactions take place on the substrate during the matrix formation. The rate of formation of the various clusters depends not only on the concentration of the metal atom but primarily on actual temperature of the outer layers of argon. From the fact that there is no asymmetry in the intensity of the components of the quadrupole doublets, we conclude that the trimers and dimers are *randomly oriented*, invoking a relatively deep zone for reaction (reaction zone) containing several layers of argon, which allows for random orientation of the clusters. By inspection of the three different samples in Table I, it can be seen that the sample with 0.38 at. % Fe and 0.26 at. % Sn has the lowest concentration of monomers and dimers both of Sn and Fe, suggesting a high yield for trimers. The reason for the relatively high depletion of the small clusters is probably due to a slight overheating of the sample as

compared to the others. This is further evidence that reactions taking place in the matrix are governed primarily by the temperature of the outer layers which determines the mobility of the atoms.

Concerning the reactivity and affinity to form the various clusters one notes the following:

(a) Independent of the Fe-to-Sn ratio, the occurrence of Fe₂ is higher than FeSn, suggesting a higher reactivity for Fe+Fe→Fe₂ than for Fe+Sn→FeSn formation.

(b) More trimers of FeSn₂ than of Fe₂Sn and Fe₃ are formed, independent of Fe-to-Sn ratio. This suggests that the reactivity for Fe+Sn₂→FeSn₂ or FeSn+Sn→FeSn₂ formation is higher than that of Fe₂+Sn→Fe₂Sn, FeSn+Fe→Fe₂Sn, or Fe₂+Fe→Fe₃. In general, the formation of tri-iron clusters is exceptionally rare.

(c) The SnFeSn clusters are more abundant than the FeSn₂ clusters, suggesting that the FeSn+Sn→SnFeSn or Fe+Sn+Sn→SnFeSn reactions are more favorable than the Fe+Sn₂→FeSn₂ ones.

CONCLUSION

By combining the hyperfine-interaction constants and relative intensities of the absorption peaks we were able to characterize the various dimers and trimers of Fe-Sn formed in an argon matrix. Despite low metal concentration a large fraction of trimers and dimers are formed in a zone close to the surface. There is a distinct preference for the formation of iron-tin trimers with Sn excess, independent of the relative concentrations of Fe-Sn. The cluster identification and their structural assignments were based primarily on qualitative arguments. Undoubtedly a more quantitative approach based on self-consistent clusters calculations is needed. Nevertheless, we hope that the present results will provide a basis for small cluster calculations, not only to explain the various configurations, but also the preference for certain reactions taking place between monomers and dimers of heteronuclear atoms.

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