

# Mössbauer isomer shifts of $^{119}\text{Sn}$ in metals and alloys

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The Mössbauer isomer shifts ( $S$ ) of  $^{119}\text{Sn}$  were measured in homogeneous metal matrices, in certain binary alloys, and in intermetallides. The main property that determines the behavior of  $S$  for Sn atoms in metallic systems is the locality property, which reflects the dominant contribution of the interaction with the nearest neighbors and the observed changes of the electron density. A linear correlation between  $S$  and the electronegativity  $\varphi_M$  of the matrix was obtained for Sn atoms admixtures in pure metals. The drastic weakening of the dependence of  $S$  on  $\varphi_M$  for transition metals is due to the decrease of the  $s$ -component of the wave function as a result of  $sd$  hybridization. The nonlinearity of the dependence of  $S$  on the composition in binary alloys is interpreted with the aid of a model in which account is taken of the inhomogeneous electron-density distribution, due to the difference between the energies of Sn-atom bonds with neighboring atoms of various types. We discuss the significance of these results to the interpretation of data on magnetic hyperfine interaction of Sn atoms with metallic magnetics.

## 1. INTRODUCTION

One of the most important parameters measured in Mössbauer spectroscopy is the isomer shift (IS) of a resonance line. The IS is proportional to the electron density in the region of the nucleus. The value of the IS is highly sensitive to changes of the configuration of the atom's valence electrons. The IS is therefore widely used to study the electron structure of solids. By measuring the IS of a metallic system it is possible to investigate the electron-density distribution changes that reflect the features of the interaction between the atoms when an alloy or an intermetallic compound is formed (see, e.g., Refs. 1 and 2).

The study of the IS of  $^{119}\text{Sn}$  impurity atoms in homogeneous metallic matrices is the subject of many studies made mainly during the early development of Mössbauer spectroscopy. (The main results of these studies and a bibliography can be found, for example, in Flinn's review<sup>2</sup>.) Certain relations were established, in the form of correlations between the magnitude of the IS and such matrix-metal properties as the atomic volume, the compressibility, the Debye force, and others. Unfortunately, none of these correlations have been thoroughly interpreted. The question of the factors that determine the value of the IS for Sn atoms in metals remained unanswered even empirically. It is easily seen that by a mere determination of the above-mentioned correlations contributes little to the solution of this problem. The main characteristic properties of pure metals are known to depend in like fashion on the place of the element in the periodic table, so that all these properties strongly correlate with one another. The existence of a correlation between the IS and some property of a matrix metal is therefore almost trivial and reflects in the main only a general interrelation between various properties of metals. It should also be noted that sufficiently pronounced correlations were obtained only for Sn impurity atoms in nontransition metals. This is partially attributed to the incomplete accuracy of the experi-

mental data, and also to the fact that most properties of transition-element matrix metals taken as a group vary in a relatively narrow range.

The isotope  $^{119}\text{Sn}$  is widely used in Mössbauer spectroscopy as a probe to study the electronic and magnetic structures of metallic systems. The measured values of the IS contain important information both on the properties of the system and on the features of the interaction between the Sn impurity atom and the matrix atoms. Unfortunately, an appreciable (and the most important) part of this information cannot be extracted from experimental data, since there are no specific data on the relation between the observed values of the IS and the parameters of interest. An experimental determination of the main factors that determine the value of the IS for Sn atoms in metallic systems is therefore most urgent. Interest in this problem is increasing in view of the recently observed correlation between IS and hyperfine fields for Sn impurity atoms in gadolinium intermetallides.<sup>3</sup> It was shown that in a number of cases the observed parameters of the magnetic hyperfine interaction reflect directly the features of the chemical interaction. One can expect a correct interpretation of the IS data to be useful for elucidation of the nature of the mechanism that transfers the spin density from magnetic atoms to nonmagnetic ones in metallic magnetics.

We have carried out systematic measurements of the IS for  $^{119}\text{Sn}$  in metals, binary alloys, and some intermetallic compounds, having crystal structures typical of metallic systems. All the IS measurements were made under identical conditions: at 77 K relative to a  $\text{CaSnO}_3$  source kept at room temperature. The measurements were made with spectrometers operating in a constant-acceleration regime. In most cases, a double spectrometer<sup>4</sup> was used, which permitted highly accurate measurements of the relative shifts of the Mössbauer lines. As a rule, the absolute values of the IS were measured with accuracy not worse than 0.02 mm/s; the relative measurements of the IS in binary alloys were measured

TABLE I. Isomer shifts for  $^{119}\text{Sn}$  impurity atoms in metallic matrices.

Matrix metal	$\varphi$ , arb. un.	Tin-impurity density, at. %	$S$ , mm/s	References	Matrix metal	$\varphi$ , arb. un.	Tin-impurity density, at. %	$S$ , mm/s	References
Nontransition metals					Transition metals				
Al	4.20	$\leq 0.1$	2.33(2)	[8]	Ti	3.65	0.3	1.73(2)	[10]
Cu	4.55	0.5	1.78(2)		V	4.25	0.3	1.66(2)	
Ga	4.10	0.1	2.57(2)		Cr	4.65	0.5	1.58(3)	
Ag	4.45	0.3	2.14(1)		Mn	4.45	0.5	1.69(3)	
In	3.90	0.2	2.92(1)		Fe	4.93	0.6	1.58(2)	
Sn	4.15	—	2.59(1)		Ni	5.20	0.3	1.57(2)	
Au	4.50	0.8	2.08(2)		Y	3.20	0.4	1.97(2)	
Tl	3.90	0.8	3.00(2)		Zr	3.40	0.5	1.72(2)	
Pb	4.10	0.7	3.11(1)		Nb	4.00	0.2	1.67(2)	
Bi	4.15	1.0	2.64(3)		Rh	5.40	0.2	1.47(2)	
				[9]	Pd	5.45	0.5	1.53(2)	[13]
					La	3.05	0.2	1.97(2)	
					Gd	3.20	0.5	1.91(2)	
					Hf	3.55	0.3	1.78(2)	
					Pt	5.65	0.4	1.32(3)	

Remarks. The isomer shifts  $S$  were measured at 77 K relative to a  $\text{CaSnO}_3$  source kept at room temperature. 2. Absence of a reference in the last column of the table means that the result was obtained in the present paper.

accurate to 0.005 mm/s. To decrease the probability of the onset of short-range order, quenched alloys were used; the intermetallides were annealed to fit the phase diagram. To interpret the data we used also certain results obtained earlier by others. Some of these results were reduced to standard conditions in accordance with the recommendations formulated in Ref. 5. In particular, it was assumed that the shifts measured with  $\text{CaSnO}_3$  and  $\text{BaSnO}_3$  sources are experimentally indistinguishable. For certain matrices, (e.g., Zn and Cd), the data obtained by different workers are contradictory (probably because of metallurgical difficulties): these data were disregarded. The values of the IS for the Sn atoms in homogeneous metallic matrices and in intermetallides are listed in Tables I and II, respectively. Table I contains also data on the density of the impurity tin in the investigated metals.

## 2. IMPURITY Sn ATOMS IN HOMOGENEOUS METALLIC MATRICES

The problem of interpreting the IS in metals and alloys is closely connected with the problem of the binding energy of atoms in metallic systems. The difficulties encountered in the solution of this problem are universally known; they are due primarily to the fact that the binding energies of atoms in metals are comparable with energies of the atomic excitations and are not small compared with the ionization energies. The analysis of the empirical and semi-empirical experimental data is made substantially simpler by considering not the absolute values of the binding energies, but only the differences between the binding energies in the alloys and in the corresponding pure metals.<sup>6</sup> A similar approach must be used also to the IS: the electron densities corresponding to the observed values of the IS must be compared not with the electron density in the free atom (or in the free ion), but with the electron density in the metallic system, which can serve as a convenient origin for the IS scale. In this case (at least

when considering IS for Sn impurity atoms in nontransition metals), this origin is the value of the IS in metallic tin ( $\beta$ -Sn).

In such an approach to the analysis of the experimental data, an important factor that determines the variation of the IS within a group of similar system, is the electronegativity difference  $\Delta\varphi = \varphi_M - \varphi_0$ , where  $\varphi_M$  is electronegativity of the matrix metal and  $\varphi_0$  is the electronegativity of the metal used as the reference (metallic tin in our case).<sup>1</sup> It must be borne in mind that electronegativity is not an exact quantitative property of an element. In particular, can be altered by substantial changes of the electron configuration of the atom. An important condition for a correct use of the electronegativity concept is that the IS variations be considered for a limited system group for which the electron configuration of the given atom can be regarded as relatively stable. Under this condition one can expect the isomer shift  $S$  for an impurity atom in a homogeneous metallic matrix to be connected with  $\Delta\varphi$  by the simple linear relation<sup>1</sup>

$$S = S_0 + B\Delta\varphi, \quad (1)$$

where  $S_0$  is the value of the IS in the metal used as the reference, and  $B$  a coefficient constant for the given group of systems.

As already noted above, the electronegativity is only an approximate quantitative characteristic of the element. In practice one uses several electronegativity scales obtained by using different properties of the atoms, metals, and chemical compounds. These scales are on the whole analogous, but differ from one another in details. (An interesting discussion of this equation, and a comparison of electronegativity scales are given in Refs. 7.) To analyze the experimental data, we used the Miedema scale<sup>6</sup> based on data on the work functions of metals and on the results of analysis of the binding energies in binary alloys. We assume that this scale agrees

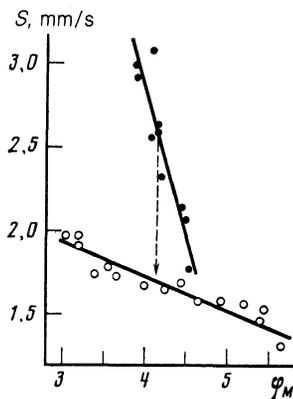


FIG. 1. Isomer shift  $S$  for  $^{119}\text{Sn}$  impurity atoms in metals vs the electronegativity  $\varphi_M$  of the matrix. (Dark and light circles—nontransition and transition metals, respectively.) The solid lines correspond to the linear relations (2) and (3). The vertical arrow shows the change of  $S$  for two groups of matrices at  $\Delta\varphi = \varphi_M - \varphi_{\text{Sn}} = 0$ .

best with the real situation in alloys. An exception is the value of  $\varphi$  for Au. The high value of  $\varphi$  for Au in the Miedema scale is indicative of an interaction of Au with transition metals (with participation of the  $d$ -electrons of the Au atom). At the same time, the Au–Sn interaction is similar to the Ag–Sn and Cu–Sn interactions, i.e., is typical of nontransition-element interactions. The value  $\varphi = 4.5$  assumed by us for Au agrees best with this rule. The values of  $\varphi$  for nontransition and transition metallic matrices are given in Table I.

The dependence of the isomer shift  $S$  of impurity Sn atoms in metals on the electronegativity  $\varphi_M$  of the matrix is shown in Fig. 1. It can be seen that the experimental data are distinctly divided into two groups (nontransition and transition metals); within each of these groups, good agreement is observed between the data and relation (1). (Noticeable deviations of the values of  $S$  in certain matrices from this linear relation should be attributed to the somewhat arbitrary character of the electronegativity scale.) The possibility of representing the experimental data by Eq. (1) confirms that, within the limits of each of the two groups of matrices, the electron configuration of the Sn atom is indeed relatively stable and the observed changes of  $S$  are determined by the spatial electron-density shift that depends on the difference  $\Delta\varphi$ . As expected, the electron density in the region of the Sn nucleus decreases with increase of  $\varphi_M$ . The functional form of the dependence of  $S$  on  $\varphi_M$  does not change when the sign of  $\Delta\varphi$  is reversed (i.e., it is independent of the sign of the electron-density transport).

The experimental data were reduced by least squares in accordance with Eq. (1). For the Sn impurity atoms in nontransition metals we obtained the following relation between  $S$  and  $\Delta\varphi = \varphi_M - \varphi_{\text{Sn}}$ :

$$S[\text{mm/s}] = 2.59 - 1.74\Delta\varphi. \quad (2)$$

A feature of this group of data is a very strong dependence of  $S$  on  $\Delta\varphi$ , which indicates a large contribution of the  $s$  component to the wave function of the valence electrons of the Sn

atom in nontransition metals. According to an estimate obtained in Ref. 15, the configuration of the valence electrons of the Sn atom in metallic tin can be approximately represented as  $s^{1.7}p^{2.3}$ . The range of the effective number  $n_s$  of the  $s$  electrons can be roughly estimated by using a semi-empirical formula for the dependence of  $S$  on the configuration of the valence electrons of the Sn atom.<sup>2</sup> According to this formula, the derivative  $dS/dn_s$  is approximately equal to 3 mm/s per  $s$  electron. Thus, the range of variation of the IS for Sn atoms in nontransition metals (from 1.78 to 3.11 mm/s) corresponds to a variation of  $n_s$  from 1.4 in a Cu matrix to 1.9 in a Pb matrix. It must be borne in mind, however, that these estimates are tentative, give an idea of the change of the electron density in the region of the nucleus, but apparently do not represent the real change of the electron configuration. As already noted, it is natural to regard the variations of the IS within a given group of matrices as the result of a spatial shift of the electron density, due to a difference between the electronegativities, under conditions of relative stability of the electron configuration of the Sn atom.

For Sn impurity atoms in transition metals, a similar reduction of the data leads to the following relation between  $S$  and  $\Delta\varphi$ :

$$S[\text{mm/s}] = 1.7 - 0.2\Delta\varphi. \quad (3)$$

From this equation (and from Fig. 1) it can be seen that for transition matrices (compared with nontransition ones), a drastic decrease is observed both in the value of  $S$  at  $\Delta\varphi = 0$  and in the dependence of  $S$  on  $\varphi_M$ . (As a result, the values of  $S$  in these matrices vary in a relatively small range, notwithstanding the large range of variation of  $\varphi_M$ .) The change of the coefficients of Eq. (1) means that the configuration of the valence electrons of the Sn atom in transition metals has substantially changed; particularly typical is the drastic decrease of the derivative  $dS/d\varphi_M$ . This result means a strong decrease of the  $S$  component of the wave function of valence electrons, which can be naturally attributed to  $sd$  hybridization resulting from the interaction of the valence orbitals of the Sn atom with the  $d$  states of the transition-metal atoms. It should be noted that the change of the total effective number of  $s$  electrons for the two groups of matrices is not so large, whereas the derivatives  $dS/d\varphi_M$  change by almost a decade. This means that the main part of the  $s$ -electron density of the Sn atom is always well localized and does not change so strongly when the alloy is formed. A substantial change takes place in only a small part of the  $s$ -electron density, located at distances of the order of the Wigner-Seitz radius. This conclusion agrees well with the results of the relativistic calculation of the radial dependence of the density of the valence electrons of the Sn atom in  $\beta$ -Sn (Ref. 16), according to which not less than 90% of the  $5s$ -electron density is localized within the Wigner-Seitz cell.

The results of this analysis show, in particular, that it is possible in principle to classify metallic systems (alloys, intermetallics) in accordance with the stability of the electron configuration of the Sn atoms (impurity atoms or atoms entering in the system as a natural component). It can be assumed that all such systems can be subdivided into groups

TABLE II. Isomer shift  $S$  for  $^{119}\text{Sn}$  in copper intermetallics ( $N$  is the number of nearest neighbors of the Sn atom,  $r$  is the distance between the Sn atom and its nearest neighbors).

Matrix	Type of Structure	$N$	$r$ , Å	$S$ , mm/s	References
Cu	$A1$	12	2.56	1.78(2)	
$\text{Cu}_3\text{Sn}$	$\text{Cu}_3\text{Sn}$	12	2.69–2.77	1.82(2)	
$\text{Cu}_4\text{MnSn}$	$C15$	12	2.89	1.77(2)	
$\text{Cu}_2\text{MnAl}$ (Al site) <sup>1</sup>	$L2_1$	8	2.58	1.77(5)	[18]
$\text{Cu}_2\text{MnSn}$	$L2_1$	8	2.67	1.79(5)	[18]
$\text{CuMnSb}$ (Sb site)	$C1_b$	4	2.64	1.80(1)	

Remarks. 1. The isomer shifts  $S$  were measured at 77 K relative to a  $\text{CaSnO}_3$  source kept at room temperature. 2. Absence of a reference in the last column of the table means that the result was obtained in the present paper.

with fixed pairs of numbers  $S_0$  and  $dS/d\varphi_M$ , where  $S_0$  is the value of the IS for a real or hypothetical system corresponding to  $\Delta\varphi = 0$ . For Sn impurity atoms in homogeneous metallic matrices, two such groups were singled out (nontransition and transition metals); clearly, however, the number of such groups can also be much larger. For example, for one of such groups the “reference point” should be grey tin ( $\alpha\text{-Sn}$ ), for which  $S \approx 2$  mm/s. Such a classification may be of interest, for example, from the standpoint of comparing the features of a chemical interaction and the structure of intermetallic compounds.

### 3. LOCALITY OF IS FOR Sn ATOMS IN INTERMETALLIDES

Important regularities, which characterize the IS for Sn atoms in metallic systems, are revealed by the study of ordered alloys and intermetallics. It was noted earlier<sup>3,7</sup> that the IS for impurity Sn atoms in gadolinium alloys changes very little when the structure and composition are changed. In the present study we measured the IS for  $^{119}\text{Sn}$  in a group of copper intermetallics having different compositions and different crystal structures. We chose compounds in which the nearest neighbors of the Sn atom were exclusively Cu atoms, but their number varied in a wide range. The structures of the investigated compounds were typical of systems with metallic-type bond. The results of these measurements are given in Table II.

It can be seen that the IS is highly constant and is independent of the composition of the compound, of the crystal structure, and of the number of nearest neighbors. In all cases the IS is practically the same as for Sn impurity atoms in pure copper. This shows clearly that the IS for Sn atoms is a local characteristic determined by the type of neighboring atoms and not dependent (or weakly dependent) on other parameters. In particular, a parameter such as the average electron density is certainly not significant. Attention is called in particular to the independence of the IS of the number of nearest neighbors (which varied in the investigated system in a wide range, from 4 to 12). At first glance, this property of the IS seems unexpected, but it is in fact natural because of the local nature of the IS and the delocalization of the valence electrons of the Sn atom within the unit cell. The observed value of the IS must be regarded as an average over all possible bonds between the Sn atom and its nearest neighbors.

At a fixed number of valence electrons of the Sn atom an increase of the number of nearest neighbors increases the number of these bonds and decreases correspondingly the electron density per bond. It seems obvious that in this case the averaging result should not depend on the number of nearest neighbors (if they are all equivalent). This conclusion should be correct for any group of systems with metallic type of bond.

More difficult to explain is the unexpectedly weak dependence of the IS on the distance to the nearest neighbors (which is just as clearly manifested in gadolinium intermetallics<sup>3,17</sup>). As seen from Table II, for the systems investigated this distance varies in the wide range from 2.56 to 2.89 Å. It is usually assumed (see, e.g., Ref. 1) that in the interpretation of the IS for impurity atoms in metals account must be taken of the “volume effect” due to the different atomic volumes of the impurity and matrix atoms. It can be seen, however, that the IS of Sn atoms in copper alloys is the same, with high accuracy, whether the Sn atoms are impurities or not. We expect from general considerations some dependence of the IS on the volume, but for the Sn atoms both dimensional factors (the “volume effect” and the direct dependence of the IS on the distance) exert no measurable influence on the IS in the investigated systems.

### 4. IS FOR Sn ATOMS IN BINARY ALLOYS

Further confirmation of the local nature of the IS was obtained from the study of the IS of Sn atoms in binary alloys. This case constitutes a new situation, in which the nearest neighbors of the Sn atoms include atoms of different type, and the number of the neighbors of one type varies with change of composition. The observed value of the IS is defined as the average over different nearest-environment configurations. Besides the locality property, these measurements revealed also selectivity of the interaction, viz., the contribution to the IS from atoms of different type is determined not only by their number but also by the energy of the interaction between the given atom and the Sn atom.

The measurements were made for disordered binary  $\text{Cu}_{1-x}\text{Rh}_x$  alloys (at impurity tin concentration 0.3 at.%) and for the quasibinary  $(\text{Cu}_{1-x}\text{Ni}_x)_3\text{Sn}$  solid solutions. In the analysis of the results we used also data obtained earlier<sup>11</sup> for  $\text{Cu}_{1-x}\text{Mn}_x$  alloys. In all these systems the Sn atom has

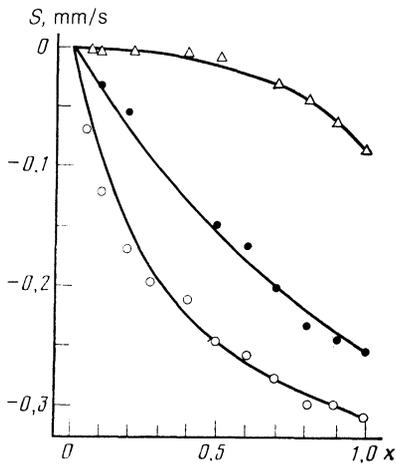


FIG. 2. Isomer shifts  $S$  for  $^{119}\text{Sn}$  in the binary alloys  $\text{Cu}_{1-x}\text{Rh}_x$  ( $\circ$ ),  $\text{Cu}_{1-x}\text{Mn}_x$  ( $\Delta$ ) and in the quasibinary solid solutions  $(\text{Cu}_{1-x}\text{Ni}_x)_3\text{Sn}$  ( $\bullet$ ). The shifts are given relative to the Cu matrix for Cu-Rh and Cu-Mn alloys and relative to  $\text{Cu}_2\text{Sn}$  for the intermetallides  $(\text{Cu}, \text{Ni})_3\text{Sn}$ . Solid lines—calculated from Eq. (6) with the values of the parameter  $\gamma$  indicated in the text. The data for the Cu-Mn alloys were taken from Ref. 11.

12 neighbors in the nearest coordination sphere. The Cu-Rh and Cu-Mn alloys have an fcc lattice. The structure of the intermetallides  $\text{Cu}_3\text{Sn}$  and  $\text{Ni}_3\text{Sn}$  has hexagonal symmetry; this symmetry is preserved also in quasibinary solutions with  $x < 0.3$  and  $x > 0.4$  (at  $x = 0.3 - 0.4$  another type of structure is produced, in which the nearest neighbors of the Sn are only Cu atoms). The measurement results are shown in Fig. 2.

The most distinguishing feature is nonlinearity of the plots of the IS vs composition, whose curvatures are of opposite sign for the Cu-Rh and CuMn alloys. It was frequently suggested earlier that for solid solutions (having the same alloy structure) the dependence of the IS on the composition should be linear; this linearity was regarded as the result of averging of the interaction for the collectivized valence electrons in the metallic system. The experimental data patently contradict this picture, but agree well with locality, considered above, of the isomer shift. The nonlinear dependence of the IS on the composition means that binary alloys preserve the individual interaction properties that determine the value of the IS in homogeneous metallic matrices. If the nearest neighbors of the atom include atoms of a different type, delocalization of the valence electrons within the limits of the unit cell does not lead generally speaking to the onset of a homogeneous distribution of the electron density. The electron density is higher in those regions of space which correspond to higher energy of the bonds between the atoms. As a result, the contribution made to the IS by the interaction with atoms of a given type is determined not only by the number of these atoms, but also by the electron density that corresponds to this interaction.

These considerations suggest a simple model capable not only of explaining the results shown in Fig. 2, but also of obtaining new information on the features of the interaction of the Sn atom with atoms contained in the investigated al-

loys. Consider a binary alloy  $\text{A}_{1-x}\text{B}_x$  and an Sn-atom nearest-neighbor configuration containing  $M$  atoms of type A and  $12-M$  atoms of type B. Assume that the IS for this configuration is the additive sum of the contribution of the individual Sn-A and Sn-B interaction. We introduce a coefficient  $\gamma$  equal to the ratio of the electron densities corresponding to the Sn-B and Sn-A interactions, and stipulate that for configurations with  $M = 0$  and  $M = 12$  the values of the IS be equal to the known values  $S_B$  and  $S_A$  in the corresponding pure metals. We assume for simplicity that the parameter  $\gamma$  is independent of composition. For the considered configuration with  $M$  atoms of type A the IS can then be expressed in the form

$$S(M) = [S_A M + S_B \gamma (12 - M)] / [M + \gamma (12 - M)]. \quad (4)$$

The parameter  $\gamma$  determines the relative strength of the bond between the Sn atom and the A and B atoms;  $\gamma > 1$  if the Sn-B interaction is stronger than Sn-A. It is convenient to rewrite Eq. (4) in the form

$$S(M) = S_A + \Delta \gamma (12 - M) / [M + \gamma (12 - M)], \quad (5)$$

where  $\Delta = S_B - S_A$ . The differences between the isomer shifts  $S(M)$  for different configurations constitute a small fraction of the width of the resonance line in the spectrum, so that one really measures the average shift, whose value for the  $\text{A}_{1-x}\text{B}_x$  alloy is

$$S(x) = \sum_{M=0}^{12} W(M, x) S(M). \quad (6)$$

For a statistical distribution of the alloy components, the probabilities of the different configurations correspond to the binomial distribution

$$W(M, x) = \frac{12!}{M!(12-M)!} (1-x)^M x^{12-M}.$$

The only free parameter of the model is  $\gamma$ , which is determined by comparing the model with experiment.

The solid lines of Fig. 2 show the dependences of the IS on the composition, calculated from Eq. (6). It can be seen that in all cases the model accounts well for the nonlinear character of the  $S(x)$  dependences. The values of the parameter  $\gamma$  in the alloys  $\text{Cu}_{1-x}\text{Rh}_x$ ,  $\text{Cu}_{1-x}\text{Mn}_x$  and  $(\text{Cu}_{1-x}\text{Ni}_x)_3\text{Sn}$  were found to be respectively 5.0, 0.25, and 1.5. This means that the Sn-Rh interaction is much stronger than the Sn-Cu interaction, which in turn is substantially stronger than the Sn-Mn interaction; the Sn-Ni interaction is stronger than the Sn-Cu interaction. (Qualitatively, as seen from Fig. 2, this follows directly from the values and signs of the deviation of the  $S(x)$  dependences from linearity.) We note that these relations between the binding energies agree with the laws governing the formation of tin-containing ordered alloys. For example, the existence of the ternary alloys  $\text{Rh}_2\text{MnSn}$  and  $\text{Cu}_2\text{MnSn}$ , in which the nearest neighbors of the Sn atoms are Rh and Cu, is accounted for by the relative weakness of the Sn-Mn interaction compared with the Sn-Rh and Sn-Cu interactions. Thus, measurement of the  $S(x)$  dependences for impurities in binary alloys

can be regarded as a method of comparing the binding energies of the atoms in metallic systems. For a quantitative interpretation of the parameter  $\gamma$  we need more detailed information on the distribution of the electron density in the alloys. This distribution depends on the features of the interaction between atoms of different types and can be highly inhomogeneous within the confines of the unit cell.

## 5. CONCLUSION

The behavior of the IS for Sn atoms in metallic systems is subject to simple rules that result from the basic locality property of the interaction that determines the value of the IS. The interaction selectivity property, considered in Sec. 4 of the present article, is particularly important for the understanding of certain features of the magnetic hyperfine interaction for Sn impurity atoms in rare-earth intermetallides. The interaction of the Sn atom with rare-earth atoms is characterized by a high binding energy. In individual cases this creates an unusual situation, in which the Sn atoms hardly interact with atoms of another type located in the nearest coordination sphere. (For the model considered above, this corresponds to very large or very small values of the parameter  $\gamma$ .) For example, there is no Sn–Mn interaction in the intermetallide GdMnSi even though the Sn–Mn distance is shorter than the Sn–Gd distance.<sup>3</sup> in  $RAI_2$  intermetallides, the IS is determined by the Sn–R interaction, although the nearest neighbors of the Sn atom are Al atoms.<sup>17</sup> These properties of the interaction between the Sn atom and its neighbors is directly manifest in the magnetic hyperfine interaction. For example, the contribution made to the magnetic hyperfine field by the  $3d$ -moment of the Mn atoms vanishes in GdMnSi.<sup>3</sup> At the same time, in the TmFe<sub>2</sub> intermetallide there is no contribution to the hyperfine field from the rare-earth sublattice, a fact explained by the relatively strong interaction of the Sn atom with Fe atoms in the nearest coordi-

nation sphere.<sup>19</sup> A joint analysis of the data on the isomer shift and hyperfine interaction uncovers thus new possibilities for the interpretation of the experimental data, on the basis of specific concepts concerning the properties of the electron-density distribution in metallic systems.

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