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ON THE MÖSSBAUER ISOMER SHIFT STUDIES OF THE ELECTRONIC STRUCTURE OF Sn IMPLANTED $A^{III}B^{V}$ COMPOUNDS

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Recent Mössbauer isomer shift (IS) measurements on ^{119}Sn impurities substitutionally implanted in several $A^{III}B^{V}$ compounds are interpreted in terms of their electronic structure. Since tin can replace both the A and the B atoms, two different IS lines arise corresponding to the donor and acceptor Sn impurities. To calculate the electronic configuration of ionized tin donors and acceptors and the relevant electron contact densities, a Green-function procedure is used based on the parametrized tight-binding approximation including relativistic wave functions. It turns out that with ionized Sn acceptors, the impurity is formed by a small cluster containing the tin atom in its neutral configuration rather than by a single negative Sn ion as might be anticipated at first sight. On the other hand, in the donor case the positive Sn ion plays the dominant role.

1. Introduction

This work represents an effort to resolve some of the problems concerning the influence of the electronic and crystal structure of the host crystal on the Mössbauer atom embedded in it. Since the Mössbauer IS is directly connected with the electronic configuration of the Mössbauer atom and can by definition be measured in solids only, it is rather frustrating to realize that the question of 'how much and in which direction free atom electron densities change in a solid', is still an open question [1].

There is no doubt that the difficulties encountered in attempting to explain the IS of impurity Mössbauer atoms are very serious. They mainly arise from three sources:

(i) The general impurity problem is still far from being completely solved, in particular with impurities in metals.

(ii) To calculate the IS [2] with acceptable precision, the electronic structure and the relevant wave functions both of the host crystal and of the impurity Mössbauer atom must be known with rather high accuracy, which often transcends the accuracy of many presently available methods for band structure calculations.

(iii) A relativistic electron density is absolutely needed even in the case where the band structure of the crystal and its chemical bond are satisfactorily described in the non-relativistic approximation. Consequently, the calculation of the electron contact density (i.e. of the electron density at the Mössbauer nucleus), which is di-

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rectly connected with the isomer shift, turns out to be a rather delicate problem with hardly assessable errors, often making the comparison between theory and experiment very uncertain.

The main reason why semiconductors make it possible to gain more specific insight into the nature of the interaction between the host and the Mössbauer impurity, is associated with their band structure:

(i) One can choose a large variety of semiconducting materials (e.g. group IV semiconductors, $A^{III}B^{V}$ compounds, etc.) having the same or very similar crystal structure, the same short and long range order, and similar band structures [3].

(ii) Slight differences in the electronegativity of the adjacent atoms in semiconducting compounds give rise to chemical bonds having different amount of ionicity.

(iii) The electronic configuration of the Mössbauer atoms sitting at substitutional sites determines whether a deep/shallow donor/acceptor configuration is formed or whether this atom enters the crystal as an isovalent impurity.

(iv) Amphoteric Mössbauer impurities make it possible to study the influence of nearest neighbours, i.e. the nature of the local chemical bond in these materials.

(v) In contrast to metals, the existence of the fully occupied valence band together with the contingent localized gap states impose certain limits on the electron charge transfer.

The measurements on the ^{119}Sn substitutional impurities in group IV semiconductors [4] showed that the isomer shift is increasing on going from diamond to silicon and germanium host crystals and further to α-tin. This increase has been interpreted [5-7] in terms of the dehybridization of the homopolar bond when going from diamond to α-tin. While in diamond the electronic structure of carbon atoms is not far from the s^1p^3 configuration, the number of the valence s-electrons Z_s taking part in the bond increases on going to Si, Ge, and α-Sn, and reaches its maximum with metallic β-tin ($Z_s \sim 1.7$) [8]; at the same time, the number of valence p-electrons Z_p is decreasing, since $Z_s + Z_p = 4$. The fact that the IS measurements [4] reflected with reasonable accuracy the directional and localized character of the chemical bond in group IV elements was very suggestive, and it was evident that similar measurements using semiconducting compounds as host crystals could provide new and independent information on the chemical bond in these materials. Above all, it was hoped that precise measurements of the IS of ^{119}Sn in $A^{III}B^{V}/A^{II}B^{VI}$ compounds might reveal the electron charge transfer between the A- and B-atoms of the respective sublattices of the zincblende crystal structure and thus contribute to the solution of a rather controversial problem of the effective ionic charge e^* in semiconducting compounds [9]. We shall see later on that, unfortunately, the results obtained come only partly up to these expectations.

The IS of ^{119}Sn sitting at substitutional sites in $A^{III}B^{V}$ compounds have been measured by Weyer and co-workers [10], and the results are presented in fig.1. Without going into details, which can be found in the references cited, considerable attention has been paid to the problem of localization of the substitutional tin impurities to ensure that only one type of lattice points (A or B) was occupied; this has been achieved by using a site-selective technique based on the implantation of radioactive ^{119}In and ^{119}Sb, respectively, which both decay in ^{119}Sn. These measurements show that in $A^{III}B^{V}$ compounds, the IS of ^{119}Sn corresponding to the donor configuration is in most cases lower than that of the acceptor configuration. We shall see later that this behaviour can be interpreted in terms of the electronic structure of the impurity ^{119}Sn atom resulting from the interaction of tin atoms with the host crystal.

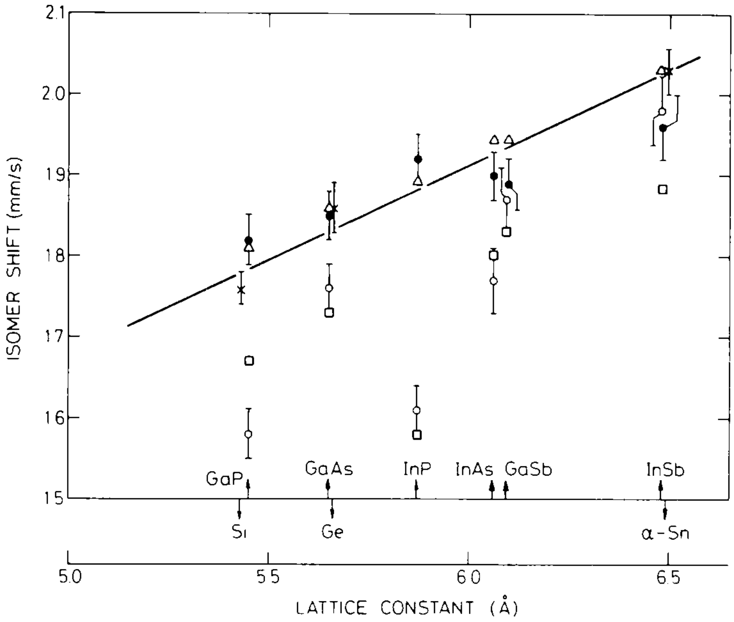

Fig.1. Experimental and theoretical values of the IS of Sn donors (o experiment, □ theory) and acceptors (● experiment, Δ theory) in $A^{III}B^{V}$ semiconducting compounds. No relaxation is assumed. See text for a more detailed explanation.

2. Mössbauer isomer shift and the electronic structure of ^{119}Sn

The Mössbauer isomer shift is usually expressed in terms of the Doppler velocity [11]

$$\delta_{IS} = \alpha[\bar{\rho}^{a}(0) - \bar{\rho}^{e}(0)] \quad , \tag{1}$$

where α is the calibration constant and $\bar{\rho}^{a}(0)$, $\bar{\rho}^{e}(0)$ represent the (relativistic) electron probability densities at the nuclei of the absorber and emitter, respectively. It has been shown in previous papers [7,8,12] that in general $\bar{\rho}(0)$ can be written as follows

$$\bar{\rho}(0) = \bar{\rho}(Z_s, Z_p, \ldots, R_{nucl}, R_A) \quad . \tag{2}$$

Here Z_s, Z_p,.. are the occupancy numbers of the valence shells of the ^{119}Sn atom (ion), and R_A denotes its effective atomic radius taking into account the finite size of the Mössbauer atom in the solid. Without going into details, which can be found in the references cited above, let us only summarize the basic idea of the procedure used in this paper.

If the Mössbauer atom forms a component of the solid, the corresponding electronic configuration as represented by the occupancy numbers can be calculated using a Green-function procedure based on the modified tight-binding method [13-17]. For example, Z_s is given as follows

$$Z_s = 2\int_{VB} n_s(E)dE = -\frac{2}{\pi}\,\mathrm{Im}\int_{VB} \langle so|G^0|so\rangle dE \quad , \tag{3}$$

where

$$G^0(E) = \lim_{\varepsilon\to 0} \frac{1}{E-H_0+i\varepsilon} \quad . \tag{4}$$

Similar expressions are valid for Z_p, etc. The relevant contact densities can be obtained using the calculated radial Dirac wave functions [18-20].

On the other hand, if the Mössbauer atom represents an impurity, the relevant Green function has to be calculated by making use of the Dyson equation

$$G(E) = G^0(E) + G^0(E)UG(E) \quad , \tag{5}$$

where U is the impurity potential [21,22]. The corresponding occupancy numbers can be calculated in analogy to eq.(3). Moreover, some additional conditions have to be respected concerning the electron-charge transfer, if any, onto the nearest neighbours. This problem will be discussed in more detail in the following section.

3. Isomer shift of substitional ^{119}Sn impurities in $A^{III}B^{V}$ compounds

Although the dehybridization of the homopolar bond as seen by the Sn impurity in Si and Ge and also in α-Sn is clearly reflected in the relevant IS values, it is evident that the differences in the IS are rather small, since the electronic configuration of the ^{119}Sn atom in all these materials is nearly the same. This situation can be markedly changed is one uses $A^{III}B^{V}$ (or $A^{II}B^{VI}$) semiconducting compounds as host crystals, since their chemical bond including more or less ionic binding has a more profound effect on the electronic configuration of the Sn impurity, and therefore on the IS. Moreover, the fact that the tin atom can exist in these materials in two different configurations, namely as a donor or an acceptor, is very important since it makes it possible to compare two theoretical values of the IS using the same band structure. On the other hand, the comparison with experiments enables us in this case to check the accuracy of the calculated electron contact densities, i.e. of the relevant wave functions.

Before proceeding to the impurity problem, let us briefly review some of the typical properties of the $A^{III}B^{V}$ semiconducting compounds which play an important role in this connection. As the unit cell of these materials includes two different atoms, it is necessary to generalize the formalism used in refs.[6-8]. Let us denote the number of the valence electrons at the relevant atoms Z(A) and Z(B), respectively. Then

$$Z(A) + Z(B) = 8 \quad , \tag{6}$$

where

$$Z(i) = Z_s(i) + Z_p(i) \quad . \tag{7}$$

$Z_s(i)$ and $Z_p(i)$ are defined by an expression similar to eq.(3), namely

$$Z_s(i) = 2\int_{VB} n_s^i(E)dE = -\frac{2}{\pi}\,\mathrm{Im}\int_{VB} \langle si|G^0|si\rangle dE \quad ,$$

$$Z_p(i) = 2\int_{VB} n_p^i(E)dE = -\frac{6}{\pi}\,\mathrm{Im}\int_{VB} \langle xi|G^0|xi\rangle dE \quad . \tag{8}$$

Index i represents the relevant valence electron wave functions corresponding to the A and B atoms, respectively. The numerical values of $Z_j(i)$ for several $A^{III}B^{V}$ compounds are given in table 1; two decimal places are specified here for the purpose of comparison rather than for the sake of the accuracy. In contrast to group IV semiconductors, the charge neutrality condition at every atom is no longer satisfied; instead of that we have to introduce the effective ionic charge e^* which is usually [9] defined in $A^{III}B^{V}$ compounds as follows

Table 1
Occupancy numbers and the relevant R_A values for several $A^{III}B^{V}$ compounds

$A^{III}B^{V}$	$Z_s(A)$	$Z_p(A)$	$Z_s(B)$	$Z_p(B)$	$R_a(A)$ (a.u.)	$R_A(B)$ (a.u.)	$U(Sn_A)$ (eV)
GaP	1.38	1.26	1.52	3.84	3.55	3.24	4.15
GaAs	1.48	1.38	1.54	3.60	3.49	3.41	3.25
GaSb	1.55	1.40	1.56	3.49	3.59	3.77	3.10
InP	1.37	1.30	1.64	3.69	3.89	3.33	3.30
InAs	1.44	1.22	1.71	3.63	3.81	3.48	3.65
InSb	1.52	1.29	1.65	3.53	3.89	3.82	2.60

No relaxation of the host crystal is assumed when calculating the $U(Sn_A)$ values.

$$3 - Z(A) = -[5 - Z(B)] = e^*/e \quad , \tag{9}$$

e^* thus represents the electron charge transferred from atom A to atom B as a result of different electronegativity of these atoms. It is to be noted that the problem of the effective ionic charge has been subject to some controversy and the literature contains many discrepancies concerning not only the value, but also the sign of e^*; moreover, this failure concerns both the experimental and theoretical results. Without going into details which can be found elsewhere [9], let us emphasize that our values of e^* depend in much the same manner as the occupancy numbers Z_j on the accuracy of the tight-binding method used and should be viewed with caution when compared with values obtained using different methods.

To illustrate the previous considerations, let us take GaAs as an example. The corresponding values of the occupancy numbers obtained with the tight-binding parametrization as given in ref.[16], are given as follows

$$Z_s(\mathrm{Ga}) = 1.48, \qquad Z_s(\mathrm{As}) = 1.54,$$
$$Z_p(\mathrm{Ga}) = 1.38, \qquad Z_p(\mathrm{As}) = 3.60. \tag{10}$$

The effective ionic charge $e^{\star}$ can be obtained from eq.(9) and amounts to $e^{\star} = 0.14$ e. The occupancy numbers for other $A^{III}B^{V}$ compounds are given in table 1.

In what follows, the donor and acceptor configuration of the tin atom will be discussed separately, since the relevant perturbation terms U in the hamiltonian H differ from each other.

3.1. ^{119}Sn donors

As ^{119}Sn donor impurity forms in $A^{III}B^{V}$ a shallow level, it is of little importance whether this level is occupied or not, the reason being, that owing to the large dielectric constant of these materials, the wave function of the electron associated with a shallow level lying in the forbidden gap is highly delocalized [23] and, accordingly, its contribution to the electron contact density can be neglected.

At first sight, the calculation of the electron contact density for $A^{III}B^{V}:Sn_A$ configurations seems to be straightforward. Once the perturbation term U is known, the respective changes $\delta Z_s(A)$ and $\delta Z_p(A)$ can be calculated and put together with the corresponding value of R_A into eq.(2). Unfortunately, the specification of the impurity perturbation term U is rather difficult since it must reflect the real situation properly. Generally, it is well-known [23] that a donor produces at a distance a screened Coulomb potential $+e/\varepsilon r$. It does not mean, however, that the donor tin impurity has the ionic configuration $Sn^{+}(5s^{2}5p^{1})$, which would correspond to a very high IS being at variance with the experiment. This, of course, raises the question of the real configuration of the donor impurity. At present, the way of determining U is mostly connected with the problem of the so-called central cell correction. Without going into details which can be found elsewhere [24], this correction is used to allow for the real Coulomb potential at the impurity cell and in its immediate neighbourhood when calculating the lowest donor state having s-character and therefore penetrating into the impurity cell more than p,d and other states. Although very many impurity potentials have been suggested [24], their explicit form cannot be used in our case since they do not take into account the electronic configuration of the impurity atom, which is of primary importance for IS considerations.

Let us now consider the electronic configuration of a tin impurity $A^{III}B^{V}:Sn_A$, which is compatible with the IS measurements. It is evident that the simplest model of an (ionized) Sn donor, producing a (screened) Coulomb potential at large distances, will have the same number of valence electrons as the A atom (ion), i.e.

$$Z(Sn_A) = Z(A) \quad , \tag{11}$$

which implies

$$\delta Z_s(Sn_A) + \delta Z_p(Sn_A) = 0 \tag{12}$$

Physically, eq.(11) means that the three valence electrons of the Sn^{+} ion behave in a similar way as the electrons of the A ion, i.e. the same charge $e^{\star}$ is transferred from Sn^{+} to the neighbouring B atoms (ions). The same charge transfer does not mean, however, that the electronic configuration is the same. In fact, the $Z_s(Sn_A)$ and $Z_p(Sn_A)$ values differ from $Z_s(A)$ and $Z_p(A)$ by $\delta Z_s(Sn_A)$ and $\delta Z_p(Sn_A)$, respectively. This change is undoubtedly small but can be seen in the IS values since the s- and p-electrons' contributions to the electron contact density noticeably differ from each other. Note that owing to the positive value of $e^{\star}$ of all $A^{III}B^{V}$ compounds in question

$$Z(Sn_A) < 3 \quad . \tag{13}$$

This inequality comes essentially from the assumption made that the electron transfer remains the same. This assumption is not the only one which could fulfill the boundary conditions. As the electronegativity of Sn is larger than that of the A atoms considered, it is possible that only a part of the charge e^* is transferred, leaving the rest of the neighbouring atoms less negative. Although the whole cluster of four B atoms, including the central donor impurity, will still produce a Coulomb field $e/\varepsilon r$ at large distances, this particular redistribution of the charge would lead to a non-zero right-hand side of eq.(12), which would in turn result in a slightly different configuration of the central tin ion. The question is whether and to what extent such an electron redistribution really takes place.

There is no doubt that formally the redistribution of the electrons around the impurity, including the nearest neighbours, could be calculated using the Green function formalism [25]. This would in our case mean to introduce two perturbation terms U(A) and U(B); as both perturbation terms contain two parameters which have to be estimated, this procedure is - as will be seen below - more complicated and inaccurate than in the case of group IV semiconductors. On the other hand, we have already mentioned that the value and sometimes also the sign of the effective charge e^* is rather uncertain even with pure $A^{III}B^{V}$ compounds, and it is evident that small changes of e^* due to the impurity would lie completely within the errors of our approximation. Another uncertainty with hardly assessable errors is due to the contingent compression of the Sn atom or to the relaxation of the host crystal around the impurity, which is unknown at the present time. Finally, the problem of d-electrons, whose contribution was neglected in our approximation, might also influence the redistribution of the electrons, especially if one realizes that the self-consistency of the whole impurity problem has to be respected.

In view of all these uncertainties, it is far more realistic to use in the first approximation a simple procedure with no, or at most a very few, adjustable parameters which would satisfactorily explain the physical situation behind the IS measurements. To this end, we shall use a procedure very similar to that outlined in the preceding paragraph, namely based on the impurity potential connected with the impurity cell only. To obtain some idea about the contingent transfer of the electron charge from/to the impurity cell, two extreme cases will be considered. The first case is identical with the model as described by eqs.(11) and (12), i.e. no additional charge transfer takes place. On the other hand, in the second case the Sn^+ ion will be considered in a configuration characterized by $Z(Sn_A) = 3$, corresponding to the case where no charge transfer to nearest neighbour B ions takes place. Which of these cases is more probable will be seen by comparison with experiment.

Our main task now is to estimate the perturbation potential U. As we are using a parametrized tight-binding method, there is no point in calculating ab initio the perturbation including the Madelung potential, etc. It is also impossible to use directly the ionization energies of the A atoms since this would not take into account the changes of their spectra due to their incorporation in the compound properly. The most natural way which is left is to use the relevant diagonal tight-binding matrix parameters corresponding to the A site, as estimated by Lowther [16]. Let us denote them E_s^A and E_p^A, respectively, while the equivalent Sn_A elements can be written in the same way as in ref.[7], although they represent, in this case, slightly different values corresponding to the donor configuration of the Sn ion. To emphasize the essential point of this approximation, let us rewrite the perturbation term in the following way

$$\begin{aligned} U &= |so\rangle\left(E_s^{Sn} - E_s^{A}\right)\langle so| + \sum_{i=x,y,z} |io\rangle\left(E_p^{Sn} - E_p^{A}\right)\langle io| + \bar{U} \\ &= |so\rangle\left[\left(E_s^{Sn} - E_s^{A}\right) - \left(E_p^{Sn} - E_p^{A}\right)\right]\langle so| + \bar{\bar{U}} \end{aligned} \tag{14}$$

Here $U = \bar{U} + E_p^{Sn} - E_p^{A}$ has to be estimated in a self-consistent way to satisfy one of the conditions mentioned above characterizing the charge transfer as given either by eq.(12) or by the condition $Z(Sn_A) = 3$. On the other hand, the first term in eq.(14) is responsible for the character of the charge transfer *within* the impurity cell, i.e. it reveals whether the effect due to the impurity will result in more or less s- and p-electrons in comparison with the occupancy numbers of the host crystal. Considering the first term in eq.(14), it is obvious that the sign of this term is determined by the difference between the modified promotion energies of the A atom and the Sn donor, respectively, as given by

$$\left(E_p^{A} - E_s^{A}\right) - \left(E_p^{Sn} - E_s^{Sn}\right) \equiv U(Sn_A) \tag{15}$$

Note that this fact is very convenient since it is well-known that the parametrization procedure within the tight-binding approximation is able to estimate the difference of E_p^A and E_s^A rather than their absolute values. To obtain some idea of the magnitude and the sign of the above expression, let us discuss GaAs:Sn_{Ga}. In this case, according to ref.[16], $E_p^A - E_s^A = 9.4$ eV. As concerns $E_p^{Sn} - E_s^{Sn}$, the problem is more complicated. If one uses the same parameters as given in ref.[15], which refer to crystalline α-Sn, we obtain $E_p^{Sn} - E_s^{Sn} = 6.92$ eV. As we have already mentioned, one should in fact use some parameters characterizing the Sn^+ configuration, e.g. the ionization energies of the Sn^+ ions; in this case, this quantity amounts to 6.4 eV. In both cases we obtain $U(Sn_A) \approx 2$-3 eV, which corresponds to the decrease of the occupancy number Z_s of the host crystal due to the Sn donor impurity and increase of the Z_p value. A similar situation is encountered in all the $A^{III}B^{V}$ compounds discussed in this paper. It has to be added, however, that the estimation of the modified promotion energy of the Sn donor is only approximate, since it does not take into account the Madelung potential properly. Moreover, the unknown effect of the compression of the tin donor of the relaxation around it can also influence the value of $U(Sn_A)$ in a hardly assessable way. To get rid of these problems, one can proceed in a very simple way and use $U(Sn_A)$ as a parameter, whose value can be estimated by accounting procedures similar to that outlined in the previous paragraph, and comparing the resulting IS values with the experiment. There is, of course, no doubt that for every A component a suitable $U(Sn_A)$ can be obtained; it would, however, be more convincing if only *one* value of $U(Sn_A)$ could be used for all A's, giving still reasonable IS values. This would namely mean that the explanation of the IS of $A^{III}B^{V}$:Sn_A is in principle correct for all $A^{III}B^{V}$ compounds, although of course some individual corrections are necessary.

This procedure has been used in both cases mentioned above; it turns out that the latter case corresponding to a Sn^+ configuration gives results which are in slightly better agreement with experiment. This implies that the nearest neighbours, having in the undisturbed crystal $B^{-e^{*}/e}$ configuration, are now less negative, with a charge equal to $-\frac{1}{6}e^{*}$. Although this result more or less corresponds to the physical situation one would generally expect, it ought to be emphasized that this rather small electron transfer and the value of the effective ionic charge e^{*} are not, unfortunately, determined with the desirable precision. To obtain definite results, it will be necessary to replace the tight-binding approximation with a more sophisticated method.

Fig.1 contains the calculated values of the IS using *one* $U(SN_A)$ value for *all* $A^{III}B^{V}$ compounds, namely $U(Sn_A) = 3.5$ eV. It can be seen that the agreement with experimental IS values is reasonably good and this seems to corroborate the physical model used. For completeness, semi-empirical values of $U(Sn_A)$ obtained directly from the experimental IS values are also given in table 1; also in this case, the condition $Z(Sn^{+}) = 3$ has been applied.

Let us finally note that our description of the tin donor is fully compatible with the Sn^{+} configuration arising from the nuclear transition as used by the site-selective technique [10]. In this particular case, the nucleus of the ^{119}In atom emits during the β-decay a fast electron, thus changing the In atom in a Sn^{+} ion

$$^{119}In \rightarrow {}^{119}Sn^{+} + \beta^{-}$$

Since the predominantly covalent bonds to the surrounding nearest neighbours are strong enough to keep the Sn^{+} ion on the lattice site, only very small changes can be expected in the chemical bond due to the increase of the nucleus charge by $+|e|$. However, the Sn^{+} ion thus created and embedded in the crystal practically in the same way as the In atom was (except for the aforementioned small changes of Z_s and Z_p), acts now in the host crystal as a donor.

It is worthwhile noting in this connection that both the recoil energy of the nucleus, resulting from the β-decay, and the sudden change of nucleus charge give rise to generation of phonons. Since the relaxation time of the crystal lattice is typically of the order of $1/\omega_D \approx 10^{-13}$ s, which is much smaller than the lifetime of the Mössbauer state of ^{119}Sn ($2.8 \cdot 10^{-8}$ s), this phonon relaxation has obviously no influence on the IS measurements.

Summarizing the Sn_A donor case, we may say that the donor is indeed formed by a positive tin ion and the electron charge transfer to its nearest neighbours, if any, is rather small. In this respect, it seems to differ noticeably from the Sn_B acceptor case.

3.2. ^{119}Sn acceptors

In principle, the acceptor configuration $A^{III}B^{V}{:}Sn_B$ can be treated in the same or similar way as the donor case. There are, however, some specific aspects connected to the acceptor-host crystal interaction which have to be discussed in more detail. To make the problem more conceivable, let us first discuss a shallow acceptor in group IV semiconductors. In this case, it is generally accepted that at very low temperatures the acceptor *atom*, sitting at a substitutional site, has a neutral configuration, while at higher temperatures it will accept an extra electron and thus form a *negative ion*. A very small activation energy in this case is due to the fact that the acceptor strives to complete the structure of the valence bonds with its nearest neighbours [26].

At first sight, it might seem that a similar situation can arise as well with tin acceptors in $A^{III}B^{V}$ compounds. Let us assume for the moment that the charge transfer takes place in the impurity cell only.

This would mean that in the former case, the tin acceptor would have a configuration $Sn^{-e^{*}/e}$, while in the latter case a configuration $Sn^{-1-e^{*}/e}$ would be necessary if the Coulomb potential of the ionized Sn acceptor at large distances should be $-e/\varepsilon r$.

To calculate the electronic configuration of ionized Sn acceptors in $A^{III}B^{V}$ compounds, it is necessary to modify the formalism used with Sn donors. To this end, it is advisable to put forward a model potential which would best characterize the physical situation at the impurity cell and around it. Is seems to us, however, that a literally taken transcription - mutatis mutandis - of the donor case might not be the most realistic one. It is namely well-known that the electronegativity of Sn is smaller than the one of the B elements, and it is therefore questionable whether a highly charged $Sn^{-1-e^{*}/e}$ ion is formed. As a tetrahedral configuration is more typical of group IV elements (like Sn, Ge, and Si) than of A and B atoms, the question arises whether the tin acceptor in a crystal with the heteropolar covalent bond will strive to preserve the tetrahedral configuration using four valence electrons only or accept extra electrons to complete the electron charge distributions, as is the case in the relevant $A^{III}B^{V}$ compound. In other words, is it the impurity or the host crystal that determines the character of the acceptor bond? It is evident that the answer to this question also determines the most suitable zero'th approximation for the perturbation approach.

Anyway, the electron configuration of the tin acceptor thus obtained must yield the IS values which are in reasonable agreement with experiment. Note that the temperature range of the present IS measurements corresponds to the ionized Sn acceptors.

Probably the best way of understanding the physical situation is to start with the electronic configuration of the tin impurity resulting from the use of the site-selective technique [10]. In this case, the electron-capture decay of ^{119}Sn produces with a high probability a neutral ^{119}Sn atom [27]. This configuration is preserved at very low temperatures; at higher temperatures, however, an electron is captured to form an ionized tin acceptor. Although these two cases resemble to some extent the behaviour of acceptor impurities in group IV semiconductors, there is a certain difference in the electronic configuration of the captured electron. While in the case of a group IV host crystal the extra electron helps more or less to form the tetrahedral configuration, in the case of a Sn_B acceptor this homopolar bond is already established using four valence electrons. As this bond is very strong, it is questionable whether a captured electron would change it markedly; moreover, a configuration of five valence electrons does not form any bond which would be stronger than the one corresponding to the tetrahedral configuration. It is therefore highly probable that during the ionization process the captured electron will be localized in the immediate neighbourhood of the impurity, predominantly at the (positively charged) A nearest neighbours, rather than directly at the impurity cell (which would correspond to a negative Sn ion mentioned previously); the distribution of this electron will probably be very similar in form to the distribution of the excess electron in an F centre. We can thus expect that in the first approximation the electron contact densities of the neutral and ionized Sn_B acceptor, respectively, will be much the same. In other words, the difference between the corresponding IS values, if any, will be rather small.

In what follows, the relevant IS values will nevertheless be calculated both for the neutral Sn_B configuration just discussed, and the $Sn^{-1-e^{*}/e}$ ion sitting at the B site in order to determine explicitly which of these configurations is compatible with the IS measurements.

Supposing that the electronic configuration of the neutral or ionized Sn acceptor is very similar to the configuration the Sn atom would have in the corresponding group IV semiconductors, it is obvious that in the first approximation the IS value of the Sn acceptor configuration in a particular $A^{III}B^{V}$ compound is equal or nearly equal to the IS value of the tin atom in the relevant group IV host crystal We can therefore expect that, e.g. the IS value of InSb:Sn_{Sb} (2.00 ± 0.05 mms^{-1}) and the corresponding value of α-Sn (2.03 ± 0.03 mms^{-1}) will agree reasonably well, which really is the case. Similarly, the IS values of GaAs:Sn_{As} (1.87 ± 0.04 mms^{-1}) and Ge:Sn (1.86 ± 0.02 mms^{-1}) are nearly identical. Now the problem arises of how to calculate the IS of the remaining $A^{III}B^{V}$:Sn_B configurations where A and B atoms do not belong to the same row of the periodic table. In this case, one can approximately estimate the IS using the mean IS value corresponding to a hypothetical compound containing the relevant group IV elements; note that a similar procedure has often been used when discussing, e.g. the trends in electronic structure and optical properties of the so-called non-horizontal sequencies of semiconducting compounds (see refs.[3,28] for more details). For example, the IS value of GaP:Sn_P can be obtained as a mean value of the IS of the following configuration

$$IS(GaP:Sn_P) = \tfrac{1}{2}[IS(Ge:Sn) + IS(Si:Sn)] \quad , \tag{16}$$

giving the value 1.81 mms^{-1} as compared with the experimental value 1.85 ± 0.05 mms^{-1}. The corresponding IS values thus estimated are displayed in fig.1. Taking into account the simplicity of this approach, using no optional parameters, the calculated values agree well with experiment. Note that to avoid additional unnecessary errors, the experimental IS values of ^{119}Sn in group IV semiconductors have been used [4].

In this connection it is worthwhile mentioning that the assumed identical configurations of the neutral and ionized Sn_B acceptor represents a convenient approximation only. As with the donors, it cannot be excluded that in the latter case a small electron transfer between the Sn atom and the nearest neighbours can take place; in particular, a small change of the number of p-electrons is probable [29]. Fortunately, their influence on the relevant IS value is rather small. There is, however, no point in calculating such a small change as long as the compression problem is open, since the contingent relaxation of the lattice around the impurity can have a more pronounced influence.

Let us now discuss the second possibility, namely that the influence of the electronic structure of the host crystal predominates, which results in a $Sn^{-1-e^{*}/e}$ configuration. To begin with, we have calculated the relevant IS values using the Z_s and Z_p values of the B atoms in the perfect $A^{III}B^{V}$ lattice; it turned out that their agreement with experiment was more or less poor. We have therefore used the same formal procedure as with donors except that the relevant diagonal matrix elements associated with atoms B have to be taken into account. It has been found that, in contrast to donors, the corresponding expression $U(Sn_B)$ [cf. eq.(15)] is negative in most cases and its absolute value is in general smaller than $U(Sn_A)$. In this way, it was possible to consider several Sn ion configurations. However, as long as the Sn ion was largely negative, the results were not very much better than in the previous case; on the other hand, for too large changes of the occupation numbers needed in the case of less charged (negative) Sn ions, our perturbation procedure ceases to be valid. It is, however, safe to conclude that the $Sn^{-1-e^{*}/e}$ ion or very similar configurations do not seem to be compatible with the IS measurements.

To answer the question we have posed at the beginning of this section, we can say that it is the tetrahedral configuration of the neutral tin impurity which is predominant in the acceptor case, since it best maintains the local chemical bond. Being interested in the electron contact density at the Sn nucleus only, we have not calculated the detailed distribution of the captured electron. Nevertheless, the localization of this electron in the neighbourhood of the acceptor implies that the ionized acceptor forms a small cluster. Therefore, when calculating the energy values of the lowest acceptor states, the central cell correction has to be taken into account; this is missing or negligible in the donor case.

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[27] As this process is more complicated than the β-decay discussed in the previous section, a comment is, perhaps, in order here. The electron capture of ^{119}Sb gives rise to a hole in the K shell while the nucleus changes into ^{119}Sn nucleus; also in this case, the sudden change of the nuclear charge and the small recoil energy bring about emission of phonons. Moreover, the K-shell vacancy is filled by an electron from a higher shell taking part either in an X-ray emission or in an Auger effect. These processes occur both in the core and in the valence band, however, in slightly different ways. While the rearrangement of the core (including the valence band electrons) proceeds in a similar way as in atoms and the relevant lifetimes are rather short (10^{-13} - 10^{-15}s), the relaxation of the holes in the valence band is more complicated. Let us add in this connection that a long-termed existence of tin ions Sn^{3+}, Sn^{2+}, and Sn^{+}, which in general would be possible in the case of free tin atoms, is avoided here due to the complete delocalization of the valence band electrons. It has been shown by E.O. Kane (Phys. Rev. 159(1967)624) and by one of the authors (EA) (Czech. J. Phys. B17(1967)953) that the lifetime of the holes in the valence band is determined both by the Auger effect and the electron-phonon interaction. It turns out that highly excited holes in the neighbourhood of the bottom of the valence band lose their energy predominantly by Auger transitions, while at lower energies (at the top of the valence band) it is the emission of optical phonons which governs the thermalization of holes. As the slowing-down times of the latter (final) process are of the order of 10^{-11} - 10^{-13}s, the total rearrangement of the electron shells around the ^{119}Sn nucleus just created occurs in times much shorter compared to the lifetime of the Mössbauer state.

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