Isomer shift and the size of Mössbauer atoms

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Although the Mössbauer effect is by definition a solid-state effect, in most cases the free-atom (ion) electronic structure has been considered when discussing the properties of Mössbauer atoms embedded in crystals. It is argued that the use of free-atom (ion) wave functions in calculation of the electron contact density at the nuclei of Mössbauer atoms in solids can lead to numerical errors, making the calibration of the isomer shift (IS) unreliable. It is shown that the allowance for the finite size of atoms in crystals has a serious influence on the value of the electron contact density. This makes it possible to introduce a new IS scheme which directly correlates the isomer shifts to the size of the Mössbauer atom for various electronic configurations corresponding to the nature of its chemical bond in the crystal. As an example, the isomer shifts for several electron configurations of ^{119}Sn atoms (ions) embedded in solids are discussed, including α-tin, β-tin, and their pressure dependence.

I. INTRODUCTION

The aim of the present paper is to contribute to the solution of a puzzling problem of calculating the electron contact densities at the nuclei of Mössbauer atoms embedded in solids, using linear combinations of free-atom (ion) wave functions. At the same time we shall try to clear up the problem of the so-called "solid-state factor" introduced rather arbitrarily to make the atomic contact densities applicable to solids.

While the latter problem is directly connected to the band structure of solids and can be explained in relatively simple terms,[1] the question of introducing quasiatomic wave functions normalized in a finite space of the crystal occupied by a "compressed" atom, might seem—at least at first sight—more controversial. The problem is that the character of the electron-density distribution around the atom in solids precludes an exact definition of the atomic radius. After all, the definition of a radius of atoms in a gaseous state is even more conflicting if not impossible. Nevertheless, it turns out that it is possible to introduce, although not in a unique way, a concept of atomic radii which can reproduce by addition the observed interatomic distances in crystals within reasonable accuracy.[2] According to the chemical nature of the solid, several types of atomic radii have been introduced: ionic radii, covalent radii, metallic, and van der Waals radii. However, the use of these radii, which are essentially based on the hard-sphere model, is predominantly restricted to crystallographic considerations, and their unjudicial use for other purposes can be misleading. A similar situation can arise when discussing the electron contact density in crystals as a function of the atomic volume. Since, moreover, the concept of atomic volumes in compounds and alloys is rather uncertain,[3] a more realistic description is desirable. We shall return to this problem in the following section.

The determination of the electron contact density at the nuclei is directly connected with the calculation of the wave functions of electrons in solids. While the description of core electrons based on the free-atom functions represents in most cases a reasonable approximation, the calculation of the valence and/or conduction electron densities is far more complicated. Among various methods used to this end, the method of linear combination of atomic orbitals (LCAO) has proven to be very useful and illustrative. In this connection, however, a problem arises, namely, whether and to what extent the use of free-atom wave functions are justified. There is no doubt that, generally, one can always construct a complete orthonormal set taking into account all overlap integrals, etc.; this procedure may, however, be rather cumbersome in practical cases, and still not precise enough for calculating electron contact densities with reasonable precision.[4] This seems to indicate that the electron contact density is more sensitive to the approximations used than some other physical quantities. For example, it is well known that the band structure of metals and semiconductors, their optical properties, etc., can be fairly accurately reproduced using the pseudopotential method. On the other hand, there is no doubt that the use of the pseudopotential wave functions for calculating the electron contact density is practically out of question. Since it is the valence electrons which are predominantly influenced by the chemical bond, the use of linear combination of free-atom orbitals in this case is rather approximative with hardly assessable errors directly carried over into the contact density. It is therefore necessary to be very cautious with this type of wave functions. On the other hand, our knowledge

of the influence of the solid on the atomic electron density is very incomplete.[5]

Although the problem of the contact densities for Mössbauer atoms forming a regular crystal is problematic enough, further complications arise in the case of impurities, both substitutional[6,7] and interstitial.[8] Also in this case the use of free-atom (ion) wave functions is rather unreliable, in particular, if the relaxation of the host lattice around the impurity is not negligible. Recently, Micklitz and co-workers[9-11] claimed that rare-gas isolated Mössbauer atoms and/or ions can provide a possibility to measure the isomer shift in their free-atom (ion) configuration. This point of view has not generally been accepted,[12] however, and we shall see later on that another interpretation of these experiments can be given which does not rely on free-atom configurations.

In the present paper we shall try to formulate the problem of calculating the electron contact densities at the nuclei of atoms embedded in solids, using self-consistent-field Dirac wave functions subjected to certain boundary conditions. It will be shown that this approach makes it possible to interpret many experimental data already in the zeroth approximation and forms—if needed—a suitable basis for more sophisticated calculations.

II. ELECTRON CONTACT DENSITY

In what follows, we shall be dealing with crystal lattices only, in which the Mössbauer atom replaces one of the atoms of the same type. This means that we shall not discuss any impurities, either substitutional or interstitial, since this has been done elsewhere.[6-8] To be specific, let us discuss the α-tin crystallizing in the diamond lattice, although a similar procedure can be used for other elemental crystals or compounds as well. This particular material, which is very often incorrectly considered as a typical example of the homopolar bond with the electronic configuration $5s5p^3$, will enable us to show the importance of the band-structure aspects, which are usually either totally neglected or misinterpreted, especially when an improper band-structure method, e.g., a simple formulation of the Wigner-Seitz method, is used.

Within the framework of the LCAO method, which is known in solid-state physics under the name of tight-binding method, the solutions of the (nonrelativistic) Schrödinger equation

$$H\Psi_{\nu\vec{k}} = E_\nu(\vec{k})\Psi_{\nu\vec{k}} \tag{1}$$

can be written in the case of α-tin in the following form:

$$\Psi_{\nu\vec{k}}(\vec{r}) = \frac{1}{\sqrt{2N}} \sum_l \sum_n e^{i\vec{k}\cdot\vec{R}_l}[C_{\nu\vec{k}}(n)a_n(\vec{r}-\vec{R}_l) + C'_{\nu\vec{k}}(n)e^{i\vec{k}\cdot\vec{\tau}}a_n(\vec{r}-\vec{R}_l-\vec{\tau})] \tag{2}$$

Here $2N$ is the number of tin atoms; $\vec{R}_l$'s are the lattice points of the first fcc sublattice of the diamond lattice, while the lattice points of the second fcc sublattice are given by $\vec{R}_l + \vec{\tau}$, where $\vec{\tau} = \frac{1}{4}a(1,1,1)$. The a_n's denote the $5s$, $5p_x$, $5p_y$, and $5p_z$ orbitals, and ν is the band index. The tight-binding method is valid under the assumption that the atoms are relatively far away from each other so that the overlap integrals are negligible, i.e.,

$$\langle a_n(\vec{r}-\vec{R}_l)|a_{n'}(\vec{r}-\vec{R}_l-\vec{\tau})\rangle = 0 \tag{3}$$

If this orthogonality condition is not fulfilled, the overlap integrals have to be taken into account properly, e.g., using the Löwdin procedure.[13] Another possibility, which would preserve the orthogonality condition, is to introduce Wannier functions instead of atomic orbitals. Both these procedures are, however, rather cumbersome and therefore very often neglected.

Since in most papers dealing with the isomer shift of α-tin, its band structure is not properly accounted for, it is very instructive to write down the wave functions corresponding to the lowest bands of the valence and conduction bands in the center of the Brillouin zone, i.e., at $\vec{k} = 0$,[14]

$$\Gamma_1: \quad \frac{1}{\sqrt{2N}} \sum_l [a_s(\vec{r}-\vec{R}_l) + a_s(\vec{r}-\vec{R}_l-\vec{\tau})] ,$$

$$\Gamma'_2: \quad \frac{1}{\sqrt{2N}} \sum_l [a_s(\vec{r}-\vec{R}_l) - a_s(r-\vec{R}_l-\vec{\tau})] , \tag{4}$$

$$\Gamma'_{25}: \quad \frac{1}{\sqrt{2N}} \sum_l [a_i(\vec{r}-\vec{R}_l) - a_i(\vec{r}-\vec{R}_l-\vec{\tau})] .$$

Here $a_i = a_x, a_y, a_z$. The nonrelativistic band-structure calculations[14] show in agreement with experiment that α-Sn is a semimetal whose lowest conduction band is degenerate at $\vec{k} = 0$ with the heavy-hole band (Γ'_{25}).

Assuming that the overlap integrals can be neglected, the electron contact density can be written as follows

$$\rho(0) = \frac{1}{N} \sum_{\nu=1}^4 \sum_{\vec{k}} |C_{\nu\vec{k}}(s)|^2 |a_s(0)|^2 = Z_s|a_s(0)|^2 , \tag{5}$$

where

$$Z_s = \frac{1}{N} \sum_{\nu=1}^4 \sum_{\vec{k}} |C_{\nu\vec{k}}(s)|^2 . \tag{6}$$

Z_s represents the mean number of the valence electrons in the crystalline α-Sn described by the wave function $a_s(r)$. A similar expression holds for Z_p. In contrast to atomic configurations, Z_s and Z_p take on nonintegral values; the normalization condition is nevertheless the same:

$$Z_s + Z_p = 4 \ . \tag{7}$$

If the contribution of d electrons would be introduced, then

$$Z_s + Z_p + Z_d = 4 \ . \tag{8}$$

Although the contribution of d electrons is not quite negligible,[1] we shall consider, for simplicity, in what follows, only the s and p orbitals. We shall see later on, however, that this apparently reasonable approximation will nevertheless introduce an error which will slightly influence the values of the isomer shift. Under the assumption that the atomic orbital $a_s(r)$ is not changed very much in the crystalline state, the difference between the atomic value $Z_s = 2$ and Z_s calculated according to Eq. (6) characterizes the change of the electronic configuration of the tin atom in the $5s$ state due to the interaction of individual atoms in the crystal. In that sense it would correspond to the so-called "solid-state factor." In general, this factor depends on the band structure of the solid in question and is, of course, different for different crystals. In our case, the form of the wave function (4) suggests that for α-tin

$$1 \leq Z_s \leq 2 \ , \tag{9}$$

where the extreme values $Z_s = 1$ or $Z_s = 2$ are fairly improbable. We shall return to this problem later on.

It is well known,[14] however, that with α-tin the spin-orbit splitting plays an important role, so that the wave functions (4) are not always quite correct and a new set of eigenfunctions including the spin functions properly has to be used. At the same time a new labeling of these functions has to be introduced, since the Bloch functions must now form a basis for the irreducible representations of the double group of the crystal. Without going into details which can be found elsewhere,[14] let us substitute the wave functions (4) by their relativistic counterparts

$$\Gamma_6: \quad \frac{1}{\sqrt{2N}} \sum_l [a_s(\vec{r}-\vec{R}_l) + a_s(\vec{r}-\vec{R}_l - \vec{r})](\substack{\alpha \\ \beta}) \ ,$$

$$\Gamma_7': \quad \frac{1}{\sqrt{2N}} \sum_l [a_s(\vec{r}-\vec{R}_l) - a_s(\vec{r}-\vec{R}_l - \vec{r})](\substack{\alpha \\ \beta}) \ ,$$

$$\tag{10}$$

$$\Gamma_7: \quad \frac{1}{\sqrt{2N}} \sum_l [a_{1/2}(\vec{r}-\vec{R}_l) - a_{1/2}(\vec{r}-\vec{R}_1 - \vec{r})] \ ,$$

$$\Gamma_8: \quad \frac{1}{\sqrt{2N}} \sum_l [a_{3/2}(r - R_l) - a_{3/2}(r - R_l - \vec{r})] \ .$$

Here, α, β are the spin functions and $a_{1/2}$ and $a_{3/2}$ are

the six p states split into two states corresponding to a total angular momentum $j = \frac{1}{2}$ and $j = \frac{3}{2}$, respectively. In the next section we shall see how all these functions can be estimated by numerical solutions of the Dirac equation, and this makes it possible to construct relativistic wave functions similar in form to the wave functions in Eq. (2).[15] The electron contact density can now be written in the following way:

$$\rho(0;Z_s,Z_p) = \sum_j |a_j(0)|^2 \ , \tag{11}$$

where the summation is over all occupied core and valence states; also in this case the valence-state occupation numbers Z_s,Z_p, etc.—in contrast to the core states—are in general fractional. In principle, the values of Z_s,Z_p should be calculated using the band structure including the spin-orbit splitting. Considering, however, that our approximation does not take into account the d states and that the spin-orbit splitting plays a significant role only in the neighborhood of the top of the valence band, we shall, for simplicity, use the Z_s and Z_p values calculated in the framework of the nonrelativistic approximation based on the parameters calculated by Chadi.[16] Using a two-point approximation,[17] the following values have been obtained

$$\alpha\text{-Sn:} \quad Z_s = 1.56, \ Z_p = 2.44 \ . \tag{12}$$

Note that these values differ slightly from the values obtained in Ref. 1, where a different band-structure model has been used, including the d states as well:

$$Z_s = 1.4, \ Z_p = 2.35, \ Z_d = 0.25 \ . \tag{13}$$

Anyway, it is quite obvious that the use of the configurations $5s^1 5p^3$ or $5s^2 5p^2$ for α-tin, as it is very often encountered in the literature,[18] is far from realistic, in particular, if these configurations should be used for calibration purposes. In fact, configuration (12) expresses the well-known fact that α-Sn is a semimetal lying between the elemental semiconductors silicon and germanium, and the metallic lead in the group IV column of the periodic table. The dehybridization of the homopolar bond when going from diamond to silicon and germanium, respectively, reaches with α-tin its maximum[1,6] and this is reflected in the Z_s value which is much larger than unity. Finally, it is worth noting that Pauling[19,20] has estimated the occupation number for β-tin, whose isomer shift is larger than that of α-tin (i.e., whose contact density is larger) as follows: $Z_s = 1.7$, $Z_p = 2.3$. Later on we shall see that these values are consistent with values (12).

From what has been said above it seems justified to conclude that a good knowledge of the band structure is necessary to obtain reliable occupation numbers and, consequently, the electron contact density. Unfortunately, it is not always easy to assess

how "good" the method is since it might reproduce some physical quantities rather well and still give bad results when calculating the electron contact density. A typical example is as it was already mentioned here, the pseudopotential method. In this connection a word of caution is perhaps in order here about the use of the simple relativistic Wigner-Seitz method which is from time to time used for calculating the contact densities. This method in its original version can be useful only for univalent metals and its application for solids with several valence electrons, as for example, tin, antimony, etc., can be rather problematic. Without going into details which can be found in Refs. 21 and 22, it is probably worthwhile to quote a recent paper by Fröman,[23] who arrived at the conclusion that even a more sophisticated formulation of the Wigner-Seitz method is not suitable for elements with more than two valence (conduction) electrons; this means that in this case the calculation of the occupation numbers Z_i is not reliable enough. Of course, this has a direct influence on the values of the electron contact density and the relevant isomer shifts although the general qualitative character of the isomer-shift—atomic-volume scheme can be reproduced reasonably well. Anyway, to obtain reliable values of the electron contact densities in solids more attention has to be given to the band-structure problem in the future.

There is another aspect of this problem which is connected with the atomic-volume approximation. Apart from the fact that with compounds the concept of the atomic volume is rather arbitrary, this approximation seems to be less suitable even for elementary solids with four or more valence electrons. Perhaps it is worthwhile to note that Pearson in his book on crystal chemistry of metals[24] has arrived at the conclusion that in these materials the atomic volume appears to be a somewhat disappointing parameter and that more useful information can generally be gained from considering interatomic distances. This is mainly due to the effects of available nonbonding orbitals or filled valence subshells. Without going into details, which can be found in Ref. 24, I should like to draw attention to the fact that in this case the isomer-shift—atomic-volume scheme might lead to erroneous conclusions, which can be fatal when used for calibration.

To demonstrate how delicate these problems are in the present case of α- and β-tin, it is of interest to mention here two papers dealing with these materials in detail. Friedman and co-workers[25] have analyzed the Mössbauer isomer shift of α- and β-tin and internal conversion data of β-tin in terms of free-atom valence-electron wave functions renormalized to the respective Wigner-Seitz radii. They arrived at the conclusion that β-Sn has 1.6 ± 0.3 $5s$ electrons while in α-Sn their number is 0.1 to 0.2 smaller, which is in very good agreement with our Z_s values men-

tioned above. On the other hand, Williamson and co-workers,[26] who were the first to study the pressure dependence of the electron contact density in a systematic way for the elements Ag through Te, were able to explain the pressure dependence of the isomer shift for β-Sn using the Wigner-Seitz model. They show that the correct value of the pressure dependence of the isomer shift is very sensitive to the value of the exchange multiplier in the Slater exchange term. Although there is no doubt that this is really the case, at least in part, the discrepancy between the electron contact densities for α- and β-tin reveals nevertheless that the problem is more complicated and very likely connected with the electronic structure of these materials. The electronic configuration assumed in this paper, namely, $5s^2 5p^2$, is very different from the real configuration and this can influence both the value of the electron contact density and its volume dependence.

We shall later on see that the isomer-shift—atomic-volume scheme can be replaced by another one based predominantly on the nearest-neighbor distance, which seems to be more suitable for solids with several valence electrons. At the same time change of the electronic structure of atoms with several valence electrons due to compression will be taken into account properly.

III. SELF-CONSISTENT-FIELD DIRAC-SLATER WAVE FUNCTIONS FOR ATOMS (IONS)

The electron contact density is not the only quantity depending rather sensitively on the size of the atoms in crystals. It is well known that the same situation arises with some other quantities, e.g., spin-orbit splitting. It was Elliot[15] and Braunstein and Kane,[27] who first pointed out that the spin-orbit splitting in solids is predominantly determined by the atomic splitting of the constituent atoms enhanced by a factor of the order of 1.5 due to the altered normalization of the wave functions in solids.

The renormalization of the atomic wave functions within the Wigner-Seitz sphere, as used in Ref. 25, represents a simple but useful approach which makes it possible to take into account the size effects of atoms in solids, at least approximately. Particularly, it is very suitable for generating an effective one-electron potential for a metal from atomic wave functions which can be used as a starting potential for more sophisticated self-consistent calculations.

Another method based on linear combination of cellular atomic orbitals has been suggested by Antoci and Mihich[28] using the intersecting-sphere model. This method proved to estimate the band structure of both semiconductors (diamond, Si, Ge) and ionic crystals (KCl, NaF, LiF) with rather good accuracy. In this connection it is interesting to note that the

idea of finite ions within the Thomas-Fermi-Dirac model was first used by Jensen[29] who calculated the lattice constant and some related parameters of several ionic crystals and obtained very reasonable results.

Taking into account the results of the methods mentioned, there is no doubt that the concept of a finite atomic size in a solid is real and useful although its quantitative specification might vary with different methods depending upon the basic assumptions made. The aim of the present method is to determine wave functions similar in form to the functions (2), in which, however, the free-atom wave functions a_j are replaced by wave functions which in a better way reflect the finite size of the atoms in solids. To this end, atomic spheres are introduced centered at each atomic site only slightly overlapping the atomic spheres around the nearest-neighbor nuclei. Accordingly, a_j's are determined as eigensolutions of the Schrödinger equation within each atomic sphere obeying appropriate boundary conditions at the sphere radius R_A and being normalized within this sphere. These wave functions will enable us to calculate the electron contact density without performing—at least in most cases—detailed band-structure calculations for various electronic configurations and size of the atoms (ions), which vary from solid to solid. Since the electron contact density includes relativistic effects, it is necessary to replace the nonrelativistic Schrödinger equation with the Dirac formalism.

The numerical values of the wave functions have been calculated using a modified version of the program written by Liberman and co-workers.[30] Assuming that inside a particular atomic sphere the potential is spherically symmetric, the major and minor components of the radial wave functions P_i/r and Q_i/r, respectively, describing the motion of the ith electron in the field of the nucleus and other electrons, satisfy the coupled Dirac equations

$$-cs\frac{dP_i}{dr}-cs\kappa\frac{P_i}{r}-c^2Q_i+V(r)Q_i=E_iQ_i \ ,$$

$$+cs\frac{dQ_i}{dr}-cs\kappa\frac{Q_i}{r}+c^2P_i+V(r)P_i=E_iP_i \ . \tag{14}$$

Here $j=l+\frac{1}{2}s$, $s=\pm1$, $\kappa=-s(j+\frac{1}{2})$, l and j being the angular momentum and the total angular momentum quantum numbers, respectively. $V(r)$ is the total potential energy, which in our approximation includes the electrostatic potential due to a finite nucleus, the Coulomb potential due to all other electrons with a tail correction, and a modified Gáspár-Kohn-Sham exchange potential.

The nuclear radius R_{nuc} is given by the well-known formula $R_{\text{nuc}}=1.2\times A^{1/3}$ fm. The wave functions are

normalized within the sphere, i.e.,

$$\int_0^{R_A}[|P_i(r)|^2+|Q_i(r)|^2]dr=1 \ . \tag{15}$$

The solutions of Eq. (14) depend, of course, on the boundary conditions imposed. While in the case of free atoms the wave functions go to zero for very large r, the same boundary conditions at the atomic sphere R_A would hardly correspond to physical reality. Since the electronic density midway between two neighboring atoms in α-tin is a rather smooth function, it is more natural to assume a constant electron density at the sphere. Since the choice of the boundary conditions is not unique and no direct experimental evidence is available, several simple possibilities have been considered. For example in Ref. 8 the major components for $5s$ and $5p$ states fulfilled the condition

$$\frac{d}{dr}\left[\frac{P_i}{r}\right]_{R_A}=0 \ . \tag{16a}$$

To get an idea of how sensitive the whole procedure is, we have chosen in the present case for $5p$ electrons another condition, namely,

$$P_i(R_A)=0 \ , \tag{16b}$$

which represents another extreme case with respect to the electron density behavior of $5p$ electrons on the atomic sphere. It turns out, however, that both models give very similar results since, in general, the influence of $5p$ electrons on the electron contact density is much smaller than that of $5s$ electrons. Since the real case lies midway between these two extremes, the problem of proper boundary conditions is studied now in more detail, particularly with regard to some other physical parameters which depend on the size of atoms as well, and which might give a better evidence than the isomer shift when compared with experiment. It should be added that the boundary conditions for the minor parts of the wave functions are chosen in accordance with conditions (16a) and (16b). It is also necessary to emphasize that although the boundary conditions used remind us of Wigner-Seitz conditions, the whole procedure has nothing to do with the Wigner-Seitz method as it is seen from the form of the wave function (2) and the relevant solution of the Schrödinger Eq. (1). Once all the wave functions are known for a particular electronic configuration and a given R_A, the electron contact density can be estimated as a mean value of the electron density over the nucleus sphere[5]

$$\bar{\rho}(Z_s,Z_p,R_A)$$

$$=\frac{3}{4\pi}R_{\text{nuc}}^{-3}\sum_i\int_0^{R_{\text{nuc}}}[|P_i(r)|^2+|Q_i(r)|^2]dr \ . \tag{17}$$

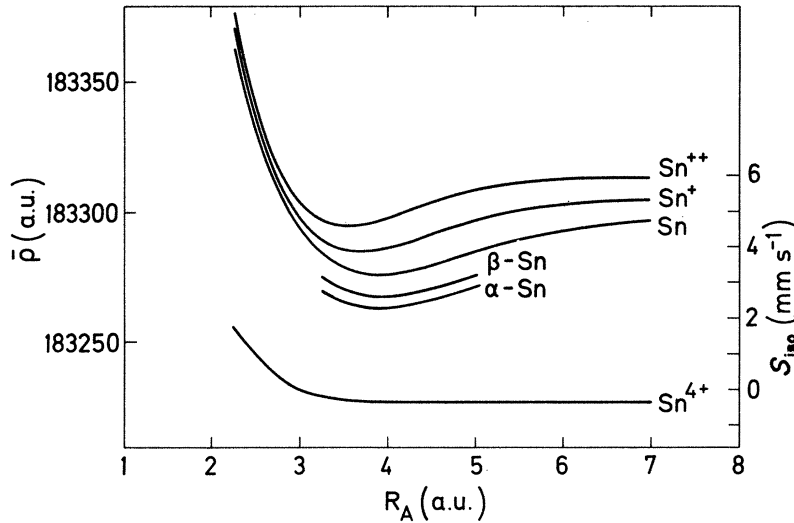It is this value which is used to calculate isomer

FIG. 1. The electron contact density $\bar{\rho}$ and the isomer shift for several electronic configurations of ^{119}Sn as a function of R_A.

shifts, etc., instead of the (nonrelativistic) value given by Eq. (5).

Figure 1 shows the dependence of $\bar{\rho}$ on R_A for several electronic configurations including α-Sn and β-Sn with Z_s and Z_p values given in the previous section. Without going into details, which will be discussed in the next section, it is evident that the introduction of the R_A dependence of the contact density $\bar{\rho}$ is essential and makes possible a more realistic description of the situation in solids than if only the limiting values of $\bar{\rho}(Z_s,Z_p,R_A = \infty)$ for free atoms or ions would be used.

IV. CALIBRATION OF THE ISOMER SHIFT FOR ^{119}Sn

The relation between the isomer shift (IS) and the electron contact densities is given for ^{119}Sn as follows[5]:

$$S_{\text{iso}} = 533(\Delta R/R)(\bar{\rho}^s - \bar{\rho}^a) = \alpha(\bar{\rho}^s - \bar{\rho}^a) \quad (\text{mm s}^{-1}) \ ,$$

$$(18)$$

where $\Delta R/R$ is the relative change of the nuclear radius, $\bar{\rho}^s$ and $\bar{\rho}^a$ are the electron contact densities of the source and absorber, and α is the calibration constant. The calibration of the isomer shift means to estimate α and/or $\Delta R/R$. To this end we shall use Eq. (18) together with isomer-shift measurements and electron-contact-density calculations for two different electronic states of the tin atom (ion). Usually, one chooses two crystalline solids with well known electronic and crystal structure, preferably with a cubic symmetry of the tin site to avoid any electric field gradient complications.[31] According to Eq. (17), the electron contact density depends both on the elec-

tronic structure as represented by the occupation numbers Z_s, Z_p, etc., and on the radius R_A of the Mössbauer atom in question.

The calibration of the isomer shift for ^{119}Sn has already been done in Ref. 8, and the following two configurations have been used.

(i) ^{119}Sn^0 atoms isolated in solid Ar, Kr, and Xe as measured by Micklitz and Barret.[9-11] The isomershift value is independent of the rare-gas matrices and amounts to 3.21 mm s^{-1} (measured at 4.2 K relative to BaSnO$_3$ source at 300 K).

(ii) The isomer-shift value $S_{\text{iso}} = -0.37$ mm s^{-1} of K$_2$SnF$_6$ (measured relative to the same source), which is supposed to correspond to Sn^{4+} ion.

The estimation of the relevant radii R_A has also been discussed in Ref. 8 in detail. As for the radii of Sn^0 atoms in solid Ar, Kr, and Xe, the corresponding radii of the rare-gas matrix have been chosen: R_A (Ar)$=3.55a_0$, R_A(Kr) $=3.70a_0$, and R_A(Xe) $=4.10a_0$. Since all these values lie in the neighborhood of the minimum of the $\bar{\rho}$ curve for Sn^0 $(5s_{1/2}^2 5p_{1/2}^2)$, respective isomer-shift values are much the same in agreement with experiment. For simplicity, the minimum value of the electron contact density for the Sn^0 configuration has been used as the first calibration point. As for the R_A value for the Sn^{4+} ion K$_2$SnF$_6$, it has been shown that its value lies practically in the region of constant $\bar{\rho}$, which was thus taken as the second calibration point. Using the corresponding values of $\bar{\rho}$ [which are slightly different from those in Ref. 8 because of the ammended value of R_{nuc} (Ref. 8) and different boundary conditions (16) used], the following calibration constant has been obtained:

$$\alpha = 0.0726, \quad \Delta R/R = 1.36 \times 10^{-4} \ .$$

These values are slightly higher than the corresponding values in Ref. 8, and reasonably agree with some recent determinations.[32-34] On the other hand, if the contact densities for $R_A = 7a_0$ (which are not too different from the values corresponding to $R_A = \infty$) are used, the relevant constants are smaller:

$$\alpha = 0.051, \quad \Delta R/R = 0.96 \times 10^{-4} \ ,$$

in agreement with previous calculations of this type.[1,11] This shows that the error due to the use of atomic contact densities can be rather large. It is therefore evident that when discussing the isomer shift of Mössbauer atoms embedded in solids, the change of the electron contact density due to the solid has to be taken into account properly.

V. ISOMER SHIFT OF α- AND β-TIN

Once the calibration constant α is known, we can calculate the isomer shift for any electronic configuration of the tin atom embedded in one or another way in solids, provided that we are able to estimate the relevant value of R_A. Figure 1 shows the R_A dependence of the isomer shift for various electronic configurations of the tin atom (ion) as calculated using the calibration constant estimated in the previous section. In this section we shall limit ourselves to two well-known tin modifications, namely, α-tin and β-tin. While α-tin is a semimetal whose crystal and band structure are very similar to those of group IV semiconductors, β-tin is a metal having a different crystal structure. Although their electronic structures differ from each other, the relevant occupation numbers given in Sec. II are not so much different. In agreement with Sec. II, in the case of α-tin we have chosen the configuration $5s_{1/2}^{1.56} 5p_{1/2}^{1.22} 5p_{3/2}^{1.22}$; due to the lack of detailed information concerning the occupation numbers of β-tin the following simple configuration has been used $5s_{1/2}^{1.7} 5p_{1/2}^{2.3}$.

In contrast to rare gases, the electron shells of atoms taking part in the covalent bond of α-tin are not closed, so that the overlap between neighboring atoms is large. This results in a relatively large bond charge in the midway region between the nearest neighbors, which is typical of the covalent bond[14] and which, unfortunately, deforms considerably the spherical symmetry of the electron charge within the atomic spheres. However, on account of the orthogonality condition the overlapping electrons cannot penetrate deeply in the ion cores of the neighboring atoms being repressed by repulsive forces. Therefore, like with ionic crystals,[8] R_A can be identified with the bond distance R_0 minus the radius of the ion of the neighboring atom R_{IN}, i.e.,

$$R_A = R_0 - R_{IN} \ , \tag{19}$$

R_{IN} representing the crystal radius of the ion as es-

timated by Pauling.[2] Millea,[35] who studied diffusion processes in homopolar semiconductors, claims that the use of the so-called univalent radii[2] in this connection gives a better agreement with experiment. Since it is very difficult to decide which of these ionic radii is better in our case, both values will be discussed and compared with experiment. It is suitable to note in this connection that the effective radius R_A cannot be larger than the half of the next-nearest-neighbor distance between two nonbonding atoms which in the α-tin amounts to $4.34a_0$. Using the values $R_0 = 5.31a_0$ and R_{IN}, as given in Pauling's book,[2] we obtain the following values: $R_A = 3.97a_0$ when using the crystal radius, and $R_A' = 3.50a_0$ when using the univalent radius of the Sn^{4+} ion. The relevant values of the isomer shift calculated according to Eqs. (17) and (18) are 2.27 and 2.43 mm s^{-1}, respectively, which is higher than the experimental value 2.10 mm s^{-1}. This is probably due to the neglect of $5d$ states when calculating the occupation numbers, which increases the Z_s value and therefore the value of the isomer shift [see the discussion in Sec. II concerning values (12)]. As both R_A values lie in the neighborhood of the minimum of the $\bar{\rho}$ curve, it is impossible to decide which approximation of the ion radii is better or more reliable.

Since the crystal structure of β-tin can be regarded as a very much deformed α-tin structure, the same procedure can be used also in this case. In β-tin, every tin atom has four nearest neighbors at a distance of $5.71a_0$ and two slightly farther away $(5.99a_0)$. We shall use, for simplicity, the nearest-neighbor distance only, i.e., $R_0 = 5.71a_0$. This gives, when using two different values of R_{IN}, the following R_A's: $R_A = 4.37a_0$ (with crystal radius R_{IN}) and $R_A' = 3.89a_0$ (with univalent radius R_{IN}). Using the calculated contact densities for a β-tin electronic configuration, as reproduced in Fig. 1, one obtains the following isomer shift values: $S_{iso}(R_A = 4.37a_0) = 2.76$ mm s^{-1} and $S_{iso}(R_A' = 3.89a_0) = 2.60$ mm s^{-1}. Taking into account both the very rough estimate of the occupation numbers Z_s and Z_p as made by Pauling,[19,20] and the uncertainty as to the values of R_A's, the agreement with the experimental value of the isomer shift 2.56 mm s^{-1} is reasonably good. Nevertheless, it is evident that a proper calculation of the band structure of β-tin and the relevant occupation numbers will be necessary for obtaining more reliable theoretical results for β-tin.

VI. INFLUENCE OF THE PRESSURE ON THE ISOMER SHIFT OF β-TIN

It is generally admitted that the pressure or volume dependence of isomer shifts represents another possibility of calibration of the isomer shift; however, both the available information and its theoretical interpre-

tation is for the present far from satisfactory.[36] Several attempts have been made to explain the "strange" behavior of the pressure dependence of the isomer shift of β-tin, which—in contrast to some other metals like Fe, Eu, etc.—shows a *decrease* of the electron contact density with *increasing* pressure.[26,37]

Before proceeding to our formulation of the pressure dependence of the isomer shift, a word of caution is suitable here. Both in Ref. 26 and in our formulation, an assumption has been made, namely, that the electronic structure (configuration) of β-tin does not change appreciably under the pressure, i.e., it is assumed that the variation of the occupation numbers Z_i characterizing the charge transfer with pressure, is negligible. While this is certainly a reasonable approximation for relatively small pressures, there is no doubt that large volume changes will cause not only changes of the wave functions but also of the occupancy numbers. This effect is probably much more important with metals where the valence electrons move relatively freely within the crystal, while in rare gas and ionic crystals only small changes of Z's can be expected due to localization of the wave functions. Anyway, the band-structure changes must be included if the phase transformation occurs. However, to include both changes properly, a series of band-structure calculations for different lattice constants would be necessary, which would complicate considerably the numerical calculations. On the other hand, as far as we are not dealing with phase transformations, one can expect that the neglect of the change of the occupation numbers will certainly not have serious influence on the qualitatively correct description of the pressure dependence of the isomer shift including the correct order of magnitude. In other words, the R_A dependence of the electron contact density for α- and β-tin in Fig. 1 has no direct physical meaning in the whole range of the R_A values but *only* in the neighborhood of the proper equilibrium R_A value, as estimated in the previous section.

Let us now turn to the problem of pressure dependence of the isomer shift of β-tin. In what follows, we shall use, for simplicity, the calibration constant as calculated in Sec. IV, although in general it would probably be more adequate to use β-tin as one of the calibration points to achieve better accuracy when studying the pressure dependence. We must, however, keep in mind that Pauling's estimate of the occupation numbers Z_s and Z_p is rather crude, so that there is no point in doing that without reliable knowledge of the relevant electronic configuration. The experimental results show[20,38] that the isomer shift change by -0.15 mm s^{-1} of β-Sn compressed by 100 kbar, corresponds to a volume reduction $(V_0 - V)/V_0 = 0.87$.[39] Since the linear change of the nearest-neighbor distance R_0 is reduced approximately by a factor of $(0.87)^{1/3} = 0.955$, one obtains for the

change of R_A the value $dR_A = -0.25a_0$. Here we have assumed that the radius of the ion R_{IN} in Eq. (19) is constant during the compression, i.e., the ion core is considered as incompressible in this case. In calculating the electron contact density $\bar{\rho}(R_A - dR_A)$ using our two values of R_A's, the relevant change of the isomer shift of β-tin takes on the value -0.11 mm s^{-1} and $+0.09$ mm s^{-1}, i.e., only in the case of the R_A radius is the calculated change of the isomer shifts in agreement with the experimental value -0.15 mm s^{-1}. Unfortunately, even in this case, no definite conclusions concerning the radii can be made since the uncertainty in the occupation numbers of β-tin is very serious, and, clearly, more detailed band-structure calculations are needed. There is, however, no doubt that precise experimental measurements of the pressure dependence of the isomer shift can help to solve this problem.

Similarly, a pressure (volume) dependence of the isomer shift of α-tin could be calculated. It turns out, however, that in this case a phase transition into β-tin takes place[40] which makes the comparison with experiment impossible. Nevertheless, it is interesting to note that for those tin compounds, whose R_A lie to the left of the minimum of the $\bar{\rho}$ curve (Fig. 1), the external pressure brings about the *increase* of the electron contact density corresponding to the increase of the isomer shift. This seems to be the case with SnMg$_2$,[38] whose isomer shift increases at first with increasing pressure and, for higher pressure decreases again due to the phase transformation. Unfortunately, the occupation numbers of SnMg$_2$ are not known, so that no quantitative conclusions can be made for the time being.

This "strange" effect, namely, that the change of the isomer shift with external pressure can be either positive or negative depending on the electronic configuration and size of the tin atom (ion) in tin compounds, seems to be found not only with tin but also with antimony, tellurium, iodine, etc.[26,41] On the other hand, recent calculations show[41] that with iron atoms (ions) the external pressure causes for all electronic configurations only an increase of the electronic contact density which leads, in agreement with experiment, to the decrease of the isomer shift, since in this case the calibration constant α is negative. In concluding this section we would like to emphasize that systematic measurements of both the isomer shift and its pressure (volume) dependence would be very desirable and helpful for establishing a reliable relation between the electron contact density or the isomer shift, and the effective size of the Mössbauer atoms embedded in crystals.

VII. DISCUSSION

In the previous sections we have formulated a new approach to the problem of the calculation of the iso-

mer shift in relation to the band structure, the electron contact density and its dependence on the size of the Mössbauer atom (ion). We have succeeded in estimating the calibration constant for ^{119}Sn and in calculating the isomer-shift values of α- and β-tin in reasonable agreement with experiment. Moreover, it was possible to explain the pressure dependence of β-tin. The objective of this section is to discuss some limitations of this method which might be important for its application to similar cases.

We have already mentioned that our wave functions represent a simple zeroth approximation which includes, however, the changes of the electron interaction due to the limited space allowed to the atom in the crystal lattice. We expect this to be a good approximation with crystals (elements or compounds) with relatively simple character of the chemical bond. In more complicated cases, e.g., when dealing with a substitutional Sn impurity, the direct interaction with the nearest neighbors must be taken into account explicitly and a more sophisticated approach is necessary.[7] It has also been shown[8] that even in the case of interstitial impurities good results can be obtained.

When calculating the isomer shift, one of the key problems seems to be the estimation of the occupancy numbers Z_i. Although in principle the way of their evaluation is rather straightforward, the numerical values of the Z's depend very sensitively on the band-structure calculations, i.e., on the method applied. It is therefore desirable to use a reliable method to calculate the occupancy numbers rather than to use, e.g., the Wigner-Seitz method, whose results, in comparison with some more recent methods, are rather poor, or cluster calculations with a small number of atoms which are not able to reproduce the band structure properly and can thus give misleading results.

Another problem, which might affect the numerical values of the contact density, is the choice of the potential in the Schrödinger equation including different forms of the exchange potential whose influence has already been discussed in Ref. 26. It turns out that both the relative and absolute values of the electron contact densities for different electronic configurations [and therefore the detailed form of the $\bar{\rho}(R_A)$ dependence] depend slightly on this choice.

Similar changes are due to various models of the nucleus charge distribution or nuclear radius R_{nuc} (e.g., for different values of r_0 in the formula $R_{nuc} = r_0 A^{1/3}$ fm in the constant nuclear-density model used in this paper). Fortunately, the uncertainties thus introduced seem to be of minor importance, especially if the calibration procedure is based on two charge states, whose contact densities differ essentially from one another. A similar effect can be expected if the Madelung potential in the crystal considered plays a significant role, in particular in the case of negative ions. All these aspects will be discussed in a later paper[41] in more detail.

Although there is no doubt that the $\bar{\rho}(R_A)$ dependence has, in the case of ^{119}Sn, the form given in Fig. 1 (and similar behavior has been found, e.g., for ^{121}Sb, ^{125}Te, ^{129}I, etc.), one has to keep in mind that both the spherical symmetry and the tentative values of the effective radii R_A represent in most cases only a crude approximation of the reality in that regions of the crystal, where the atoms (ions) overlap with their nearest and next-nearest neighbors. The direct influence of the spherical approximation in the overlap regions on the numerical values of the isomer shift is hardly assessible and evidently a systematic study of other Mössbauer atoms either in the same or similar crystals is needed to obtain more experience and evidence. Even if with other values of R_A's or different boundary conditions slightly modified results can be obtained, it is quite evident that the size of the Mössbauer atom plays, in this case, a significant role, which has to be taken into account properly. Therefore, it is very desirable if the experimental measurements of the isomer shift of Mössbauer atoms in various crystals would be systematically complemented by pressure experiments as well. This applies particularly to the isomer-shift measurements on Mössbauer atoms isolated in rare-gas matrices, which seem to represent one of the most reliable results directly comparable with theoretical calculations.

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