Systematics of ^{119}Sn Isomer Shifts in Metals

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The electronic structure of substitutional tin impurities in 38 elemental metals and semiconductors is calculated with the linear muffin-tin-orbital Green's-function method. The trends of ^{119}Sn isomer shifts in metals are discussed in terms hereof. The isomer shift shows a minimum in the middle of the transition series due to increased hybridization with the metal *d* bands, while it is largest in the *sp* metals to the right of the transition metals. Compared with the *sp* metals, the strong covalency of the group-IV semiconductors significantly lowers the isomer shift of substitutional tin atoms.

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The Mössbauer isomer shift is a widely used spectroscopy of solid-state systems on the microscopic level.[1] In conjunction with implantation techniques[2,3] this method provides valuable insight into the basic structure of elementary as well as complex defects in semiconductors[2,4] and metals.[2,5] The isomer shift ΔS is directly proportional to the density of electrons $\rho(0)$ on the nuclear position (the contact density)[6]:

$$\Delta S = \alpha[\rho(0) - \rho_{\text{ref}}(0)], \tag{1}$$

where $\rho_{\text{ref}}(0)$ is the contact density of a reference material. To improve the interpretation of isomer-shift experiments, the central question is how the characteristics of the host material influence the contact density. This is the problem addressed in the present work for the particular example of a ^{119}Sn Mössbauer atom as a substitutional impurity in elemental metals and semiconductors.

While previous studies[7] of isomer-shift trends have revealed correlations with host specific volume and electronegativity, very little is known about the microscopic causes of the variations in contact density in different solid-state environments. A mere increase in $\rho(0)$ with increasing *s*-charge character is easy to comprehend, since only *s* partial waves extend into the nuclear regime, but indirect effects on the *shape* of the *s*-charge distribution (shielding)—observed, e.g., in pressure experiments[8]—are more subtle. Recently, Akai *et al.*[9] systematically studied the ^{57}Fe isomer shift as a function of impurity Z in dilute iron alloys. They used the Korringa-Kohn-Rostoker Green's-function method and the local-density approximation and found a correlation with the *s*-electron charge transfer to the Fe atom.

This paper reports results similar in spirit to those of Akai *et al.*[9]—however, varying the host rather than the solute. The electronic structure of substitutional Sn is computed self-consistently and scalar relativistically with the linear muffin-tin-orbital (LMTO) Green's-function method[10] and the local-density approximation. This method is similar to the Korringa-Kohn-Rostoker method used by Akai *et al.*,[9] but great computational simplifications are obtained by the use of energy-independent partial waves.[10] The LMTO method gives a very good account of the electronic structure of the elemental metals[11] and semiconductors,[12] which constitute the unperturbed crystals in the present work. Trends in isomer shifts in pure crystals were previously discussed with the LMTO method.[13]

In the present calculations the perturbed region is taken to consist of the Sn impurity and the shell of nearest-neighbor Wigner-Seitz cells. Each cell is approximated by a sphere inside which the potential is assumed spherically symmetric (the atomic-sphere approximation). For computational reasons, the host crystal structure is restricted to be fcc except for those elements which take the bcc or diamond structures; e.g., the hcp metals are treated as fcc. Explicit tests show that the structural dependence of the isomer shift is small.[14] The atomic nuclei are fixed to their ideal host positions. The LMTO basis set includes *s*, *p*, *d*, and *f* waves,[11] except for the semiconductors, where only *s*, *p*, and *d* waves are used together with interstitial empty ($Z=0$) spheres.[12] The Sn core electrons are allowed to relax to the variations in valence structure. The host Green's function is calculated with the tetrahedron method[10] with 95 (55) **k** points in the fcc (bcc) irreducible wedge. All 16 (36 in diamond structure) LMTO bands of the host are included. Spin polarization was not considered in the magnetic 3*d* metals. The Sn nucleus is modeled by a homogeneously charged sphere of radius $1.2A^{1/3}$ fm and the contact density obtained as an average over the nuclear volume.

Figure 1 shows the calculated isomer shifts[15] for hosts extending from groups III*B* to IV*A* of the periodic table in the fourth, fifth, and sixth rows. Also marked are experimental values where available.[16] In addition to giving an overall good agreement with experiments, the calculations reveal a parabolic shape of the isomer-shift curve through the transition-metal series with a minimum in the middle and a maximum to the right of the series, in groups II*B* and III*A*. The parabola is rather flat in the 3*d* series, where the sequence Ti-Ni shows an almost constant Sn isomer shift. Unfortunately, to the author's knowledge, no experimental data are available for the midseries elements of the 4*d* and 5*d* series, but the wings of the parabola agree well with experimental

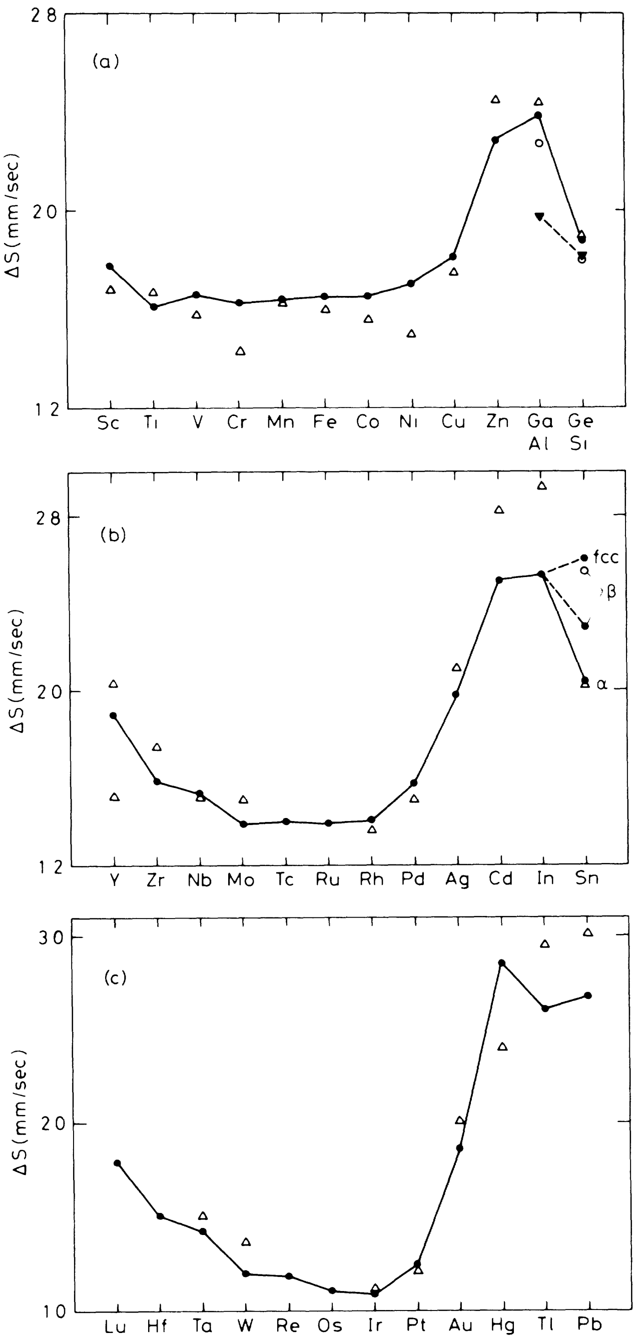

FIG. 1. (a)–(c) Calculated (solid lines) and experimental (triangles) Sn isomer shifts in the fourth-, fifth-, and sixth-row elements, respectively. In (a) the shifts (dashed line, calculated; open circles, observed) pertinent to Al and Si are also given. In (b) the shift in α-Sn, β-Sn, and a hypothetical fcc Sn metal are included. For Y, two experiments are seriously at variance.

points. The isomer shift drops again sharply from the metals of group IIIA to the diamond-structured elemental semiconductors. As for the vertical variation, the isomer shift decreases (increases) among the transition (simple) metals with higher host atomic number.

Several quantitative discrepancies between experiment and theory remain in Fig. 1. These are most probably due to nonnegligible lattice relaxations around the physical Sn impurity or precipitation alloying effects in the experiments. Calculational inaccuracies may arise from the atomic-sphere approximation. Though these are not easily assessed, I assume them small in the high-symmetry and high-coordination geometry adopted in the present work. The core contribution to the variation in electron contact density amounts to roughly (5–10)% of the valence contribution, in agreement with the conclusions of Ref. 9.

To interpret the trends of Fig. 1, I display in Fig. 2 the calculated angular-momentum–decomposed charge contents around the impurity Sn atom. To avoid the comparison of different volumes, the charge inside a sphere of *fixed radius,* taken to be 2.5 a.u., was computed. Figure 2 shows that the Sn s component of electronic charge is almost constant through the transition-metal series, whereas the p and d components peak around the middle of each series. This reflects an increasing non-s hybridization with the metal d bands, which accompany the midseries host-specific volume minima. From the Sn local density of states the p hybridization is found to be in the lower, bonding part of the d band, whereas the d hybridization extends over the whole d band. The isomer-shift behavior in the transition metals thus can*not* be understood in terms of variations in the Sn s occupancy. Rather, the pileup of non-s charge influences the *shape* of the Sn s-charge distribution though the aforementioned indirect shielding effect, to be discussed shortly. When the host s occupancy increases from the near-noble to the noble metals and further on to the Zn group, the Sn s charge also increases. This causes the *large* isomer-shift increase around the noble metals, which is further enhanced by the decrease in p hybridization. Finally, in going from the simple metallic to the covalent hosts of the diamond-structured elements Si, Ge, and α-Sn, the Sn atom adapts the host "sp^3" hybridization leading to a distinct increase in p and decrease in s charge and a drop in isomer shift. The β-Sn isomer shift falls between the shift of the covalent α-Sn structure and that of a hypothetical metallic fcc structure of Sn, in accordance with the mixed metallic covalent nature of the β-Sn allotrope. For the vertical variation in electronic structure the calculations reveal slightly decreasing Sn s charge as one goes from the $3d$ to the $4d$ to the $5d$ series. The p charges also decrease slightly, while d and f charges increase. This trend is *opposite* to the pure host s-charge variation.[11] It appears that the increased d-orbital overlap in the heavier transition-metal hosts is the dominating effect, which causes an s-to-d electron conversion on the impurity Sn atom. In the sp hosts beyond the noble metals the Sn s charge *does* comply with the host s charge.

To see the shielding effect on the isomer shift in the

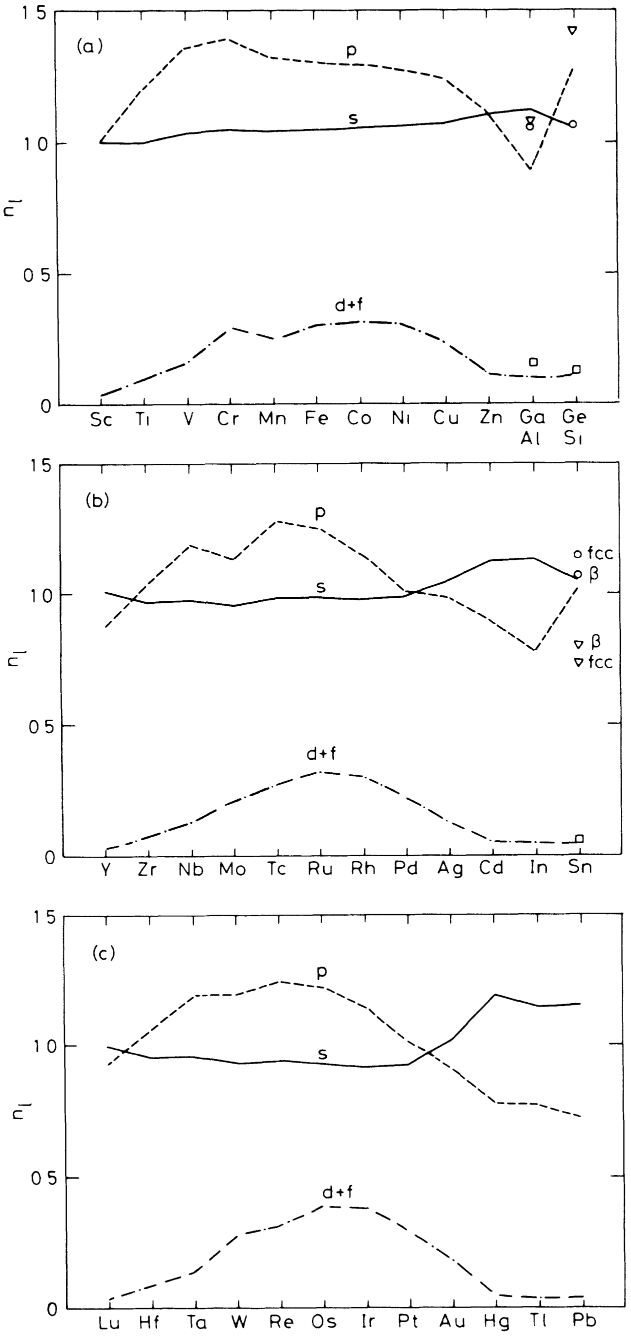

FIG. 2. (a)-(c) Calculated angular momentum weights in a sphere of radius 2.5 a.u. around the Sn impurity in hosts of the fourth, fifth, and sixth rows, respectively. Full curve, *s* electrons; dashed curve, *p* electrons; dashed-dotted curve, $d+f$ electrons. In (a) the weights for Al and Si and in (b) those of β-Sn and fcc Sn are likewise given: circles, *s*; inverted triangles, *p*; squares, *d*.

transition-metal series more explicitly I depict in Fig. 3(a) the variation in the effective one-electron potential around the Sn atom in the sequence of 5*d* hosts Hf-Au. Only the difference with respect to Pt is shown: $\Delta V(r) \equiv V_M(r) - V_{\mathrm{Pt}}(r)$. It is seen that in the midseries hosts W, Re, and Os the region farthest away from the nucleus ($R > 2$ a.u.) is relatively more favored than in Pt, while in Hf, Ta, and Au the interior ($R < 2$ a.u.) is relatively more attractive than in Pt. This is in accord with the larger non-*s* charge in the interior region in the former cases. The effect hereof on the radial *s*-charge density is shown in Fig. 3(b). Specifically, I define for host *M* the normalized radial *s*-charge density

$$\sigma_M(r) = 4\pi r^2 \rho_s^M(r)/n_s^M, \tag{2}$$

where n_s^M is the total *s*-electron count in the fixed-volume sphere [Fig. 2(c)]. Displayed in Fig. 3(b) is $\Delta\sigma(r) \equiv \sigma_M(r) - \sigma_{\mathrm{Pt}}(r)$, while Fig. 3(c) shows $\sigma_{\mathrm{Pt}}(r)$.

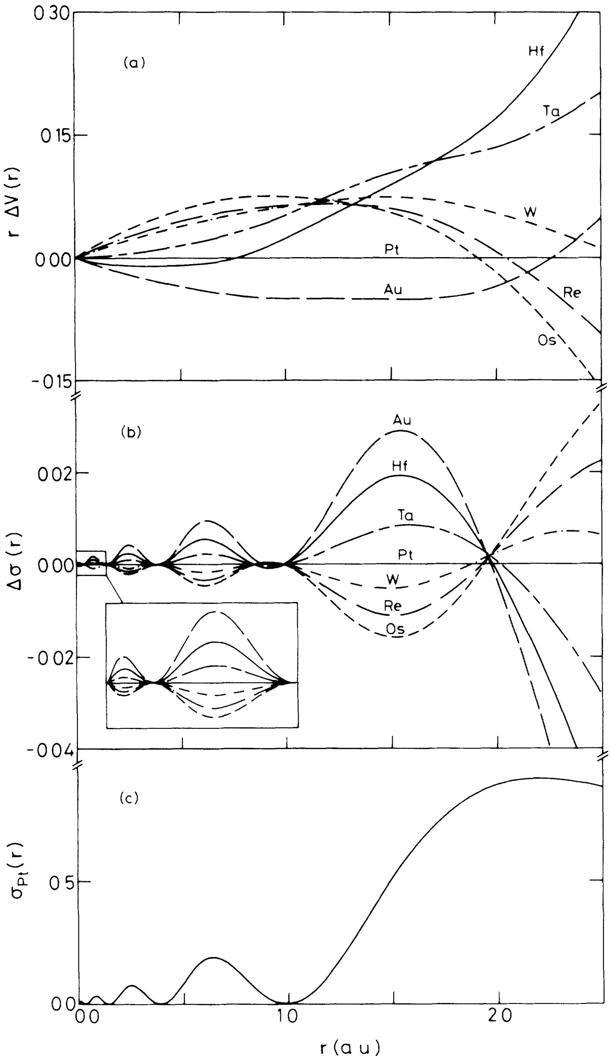

FIG. 3. Variations in (a) one-electron potential and (b) radial 5*s*-charge distribution [Eq. (2)], around a Sn impurity atom in the 5*d* hosts Hf-Au. (For clarity, Ir is left out—it lies close to Os.) Values are in atomic Rydberg units and given relative to Pt. (c) The radial 5*s*-charge distribution of Sn in Pt.

From these figures it follows that the main effect of the potential variation is the displacement of the *s*-charge maximum around $R \simeq 2.1$ a.u., which relative to Pt moves inwards in Hf, Ta, and Au and outwards in W, Re, and Os. The charge reshuffling is largest in this main hump of the 5*s* radial distribution but is mediated all the way to the origin, thus causing the variations in the contact density through the transition-metal series revealed in Fig. 1.

In summary, the ^{119}Sn isomer shifts in metals and elemental semiconductors have been investigated. A good account of experimental trends was obtained in terms of the electronic properties of the impurity. In particular the isomer-shift minima in the middle of the transition-metal series is an *indirect* effect of the host-volume minima, which leads to shielding of the Sn *s* wave, while the distinct isomer-shift increase in going from the transition metals to the simple *sp* metals is a *direct* effect of the Sn *s* occupancy increasing in the latter hosts.

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[14] The ^{119}Sn isomer shift in a host with the bcc structure is generally somewhat lower than for the same host with the fcc structure by <0.05 mm/s. Experimentally, tin in Co(hcp) and Co(fcc) differ by 0.04 mm/s (Ref. 2).

[15] In computing ΔS of Eq. (1) we used $\alpha = (0.0714 \text{ mm/s}) a_0^{-3}$ (Ref. 13) and the reference material is SnO_2.

[16] Experimental isomer shifts are (author's) averages of values reported in literature. The pertinent error bars are not easily assessed but measurements by different groups generally agree (within 0.10 mm/s), with Y an exception to this rule.