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Brief Reports

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Theoretical investigation of Mössbauer isomer shifts in compounds of Sn, Sb, and Zn

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Using the first-principles scalar-relativistic linear muffin-tin-orbital method we calculate the electron contact density in a series of crystalline solids containing Sn, Sb, or Zn as a component. The correlation with experimental Mössbauer isomer shifts is nearly perfect providing for what is believed to be the first time parameter-free calibrations of the ^{119}Sn, ^{121}Sb, and ^{67}Zn Mössbauer isotopes. The values of the relative change in nuclear radius obtained are $\Delta R/R = (1.34 \pm 0.07) \times 10^{-4}$, $\Delta R/R = (-10.4 \pm 1.0) \times 10^{-4}$, and $\Delta R/R = (7.0 \pm 1.0) \times 10^{-4}$ for the ^{119}Sn, ^{121}Sb, and ^{67}Zn isotopes, respectively.

The Mössbauer isomer shift[1] is one of the few experimental methods which investigates the electronic structure of solids on atomic scale. The technique is widely used as a spectroscopic tool to study the local chemical bond in pure crystalline materials as well as more complicated systems like impurities in solids and amorphous and implanted materials. The resonant isomer-shift velocity Δ_{IS} is given by[2]

$$\Delta_{\text{IS}} = \alpha[\rho_a(0) - \rho_s(0)], \tag{1}$$

where $\rho_a(0)$ and $\rho_s(0)$ are the electronic densities at the nuclear site (the contact density) in two different solid environments, and α is the nuclear calibration constant, which is often parametrized in terms of the relative change in the radius of the nuclear states involved, as $\alpha = \gamma \Delta R/R$, where γ is a numerical constant.[3] Extraction of the optimum information from Mössbauer isomer-shift measurements requires a reliable value for the calibration constant α of the transition used, but this has not always been available. The best way of obtaining a value of α is to compare experimental isomer shifts with calculated electron contact densities. The use of atomic calculations for the latter is widespread, but inaccurate. Recently, also molecular and cluster calculations have been reported for some isotopes, in which cases one has the advantage of being able to include the effects of the nearest-neighbor atoms on the electronic wave functions, but unfortunately boundary effects are important and not easy to assess. In the case of atomic-based calculations, one needs the assumption of an atomic configuration, which can be taken as equivalent to the actual situation in the solid (e.g., the configuration $[\text{Kr}]4d^{10}5s^15p^3$ for the tin atom in α-Sn). In the Wigner-Seitz model[4] the atom is confined to a finite sphere representing the volume allotted to the atom in the solid and, hence, the appropriate radius is introduced as a further parameter in addition to the atomic configuration. Unfortunately, the electron contact density is quite sensitive to all these choices.[5] It is the purpose of the present work to demonstrate that modern computational methods for the electronic structure of solids, including the local approximation to density-functional theory, are sufficiently accurate to allow a *parameter-free ab initio* calculation of the electron contact density of a Mössbauer nucleus in the proper solid-state environment.

The linear muffin-tin-orbital (LMTO) method[6,7] has proven a fast and reliable method for determining the electronic structure of solids, and it was adopted for the present study. It is a real- (as opposed to pseudo-) potential method, by which the crystal valence charge distribution is iterated to self-consistency. The atomic cores were treated as frozen. All effects of the crystal structure are incorporated, and relativistic effects are accounted for by the scalar-relativistic approximation,[7] in which spin-orbit coupling is omitted. Further, the LMTO method is readily applicable for a number of crystal structures, which makes it a convenient tool for calibration of Mössbauer isotopes. The present calculations included the combined correction term,[6,7] and the electron contact density was calculated as the average electron density in the nuclear volume corresponding to a sphere of radius $R = 1.2A^{1/3}$ fm. In agreement with common usage, "empty spheres"[8] were introduced in open crystal structures to facilitate a better coverage of the crystal volume. Exchange and correlation effects were treated in the local density approximation in the parametrization of Ref. 9. All calculations were performed at the experimental equilibrium volume.

Figures 1-3 display the results obtained for the ^{121}Sb, ^{119}Sn, and ^{67}Zn isotopes. The experimental[10] values for the resonant velocity Δ_{IS} are plotted versus the calculated

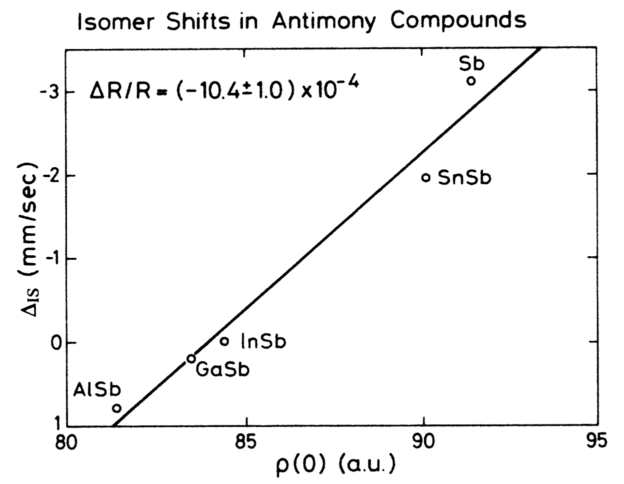

FIG. 1. Experimental isomer shifts vs calculated electron contact densities in Sb compounds. Here, AlSb, GaSb, and InSb have the zinc-blende crystal structure; SnSb is found in the NaCl structure and Sb in the arsenic structure, which is a distorted simple cubic structure.

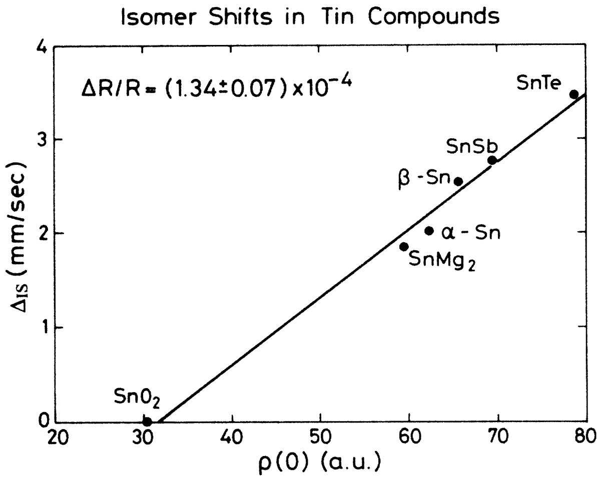

FIG. 2. Experimental isomer shifts vs calculated electron contact densities in Sn compounds. Here SnO_2 is found in the rutile structure, $SnMg_2$ in the fluorite structure, and SnSb and SnTe in the NaCl structure. α-Sn is the diamond structured allotrope of tin, whereas β-Sn is body-centered tetragonal with a two-atomic basis.

valence-electron contribution to the contact density of the crystals considered. Good linearity is found, and from a least-squares fit we derive the following nuclear calibration constants:

$$\frac{\Delta R}{R}=(1.34\pm 0.07)\times 10^{-4}\text{ for }^{119}\text{Sn},$$

$$\frac{\Delta R}{R}=(-10.4\pm 1.0)\times 10^{-4}\text{ for }^{121}\text{Sb}, \qquad (2)$$

$$\frac{\Delta R}{R}=(7.0\pm 1.0)\times 10^{-4}\text{ for }^{67}\text{Zn}.$$

The values of $\Delta R/R$ for ^{119}Sn and ^{121}Sb are in excellent agreement with the range of values reported in the literature.[11] The value of $\Delta R/R$ for ^{67}Zn has not been derived previously, but the order-of-magnitude estimate of Ref. 12 is in accordance with the value derived in the present work.

For the Sb compounds of Fig. 1, the zinc-blende-structured group-III antimonides AlSb, GaSb, and InSb are seen to fall close together with the electron contact density of AlSb lying lowest. By decomposing the crystal wave function of these three compounds into its angular-momentum character inside a sphere of fixed radius (equal to $S=3.02$ a.u.) around Sb this ordering is found to correlate with the content of p electrons: While the s-electron content of this sphere is constantly equal to 1.58 in all three compounds, the sphere contains 2.73, 2.56, and 2.53 p electrons in AlSb, GaSb, and InSb. This again reflects the slight increase of ionicity in the sequence InSb, GaSb, and AlSb in accordance with the conjecture of Pruitt, Marshall, and O'Donnell,[13] but in contradiction with the interpretation suggested in Ref. 14. The increased number of Sb p electrons in AlSb causes a shielding of the s component of the wave function away from the nuclear region with a resulting lower contact density. The effect is not large in absolute numbers but easily resolved both experimentally and computationally. The large jump seen in Fig. 1 from the group-III antimonides to SnSb and pure Sb reflects the change in bonding mechanism from tetrahedral sp^3 bonding to octahedral p^3 bonding. The effective configuration of a Sb atom in Sb metal is found to be $s^{1.85}\,p^{2.85}\,d^{0.30}$, which is not far from the s^2p^3 atomic ground-state configuration.

The Sn isomer shifts considered in Fig. 2 span a somewhat larger relative range than the Sb shifts, which is due to the incorporation of the ionic, rutile-structured compound SnO_2. The LMTO calculation for this compound reveals a significant admixture of covalency in the bonding, and this is also reflected in the valence-electron contribution to the contact density, which amounts to 30.3 a.u., or roughly half the value found in α-Sn. The jump from α-Sn to SnTe reflects the same change from zinc-blende to NaCl crystal structure as the change from InSb to pure Sb discussed above. SnSb and SnTe both have the NaCl structure, but in SnSb some promotion of Sn s electrons into bonding p orbitals occurs and, consequently, the electron contact density of Sn in this compound falls between the values pertinent to α-Sn and SnTe. In β-Sn, the metallic allotrope of tin, only reminiscences of the strong tetrahedral bonds are present and we find an electron contact density somewhat higher than that of α-Sn. The effective configuration of a Sn atom in β-Sn is found to be $s^{1.62}p^{2.04}d^{0.34}$, whereas α-Sn has an s-electron character of about 1.4–1.5.[15] These numbers are in excellent agreement with the experimental estimates of Friedman, Watson, Hodis, and Perlman.[16] Finally, in the fluorite-structured compound $SnMg_2$, Sn is the anion having a significantly larger p-electron content than in α-Sn. Also the s-electron content of Sn in $SnMg_2$ is somewhat larger than in α-Sn. This is in accordance with the eightfold coordination in $SnMg_2$. However, the shielding of the s electrons away from the nuclear region mediated by the p electrons

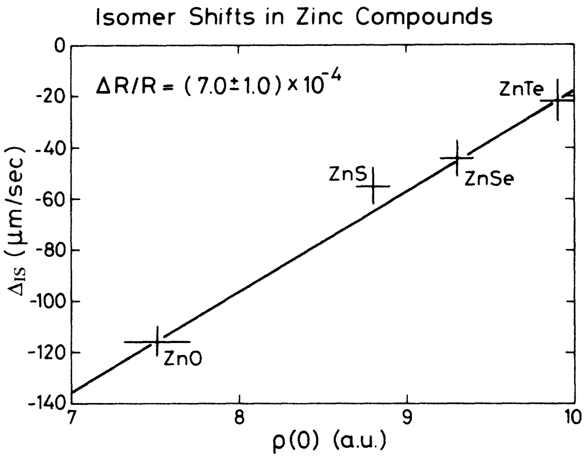

FIG. 3. Experimental isomer shifts vs calculated electron contact densities in the Zn chalcogenides. All calculations were done for the zinc-blende crystal structure.

appears to be the dominating effect, which causes a somewhat lower electron contact density of Sn in $SnMg_2$ than in α-Sn.

The 93-keV resonance in ^{67}Zn is peculiar among Mössbauer transitions in having the highest relative energy resolution[17] with a natural linewidth of only 0.31 μm/sec. Chemical shifts range over some 200 μm/sec, so considerable sensitivity is obtainable with this isotope, but due to experimental complications it has not been used so extensively as the ^{119}Sn and ^{121}Sb isotopes. The isomer shifts of the Zn chalcogenides have been measured by two groups,[12,18] which find concordant results. The measured center shifts of Ref. 12 were corrected for the second-order Doppler shift due to the zero-point motion of the Zn nucleus, and the data of this reference are used in the present work. The experimental uncertainties indicated in Fig. 3 stem entirely from this correction. The Zn contact density in ZnO was calculated in a hypothetical zinc-blende structured ZnO compound at a volume equal to the experimental equilibrium volume of wurtzite ZnO. The electron contact density has been presumed insensitive to this approximation, as the zinc-blende and wurtzite structures are very similar. This is rendered by some evidence from isomer shift measurements on ZnS in its zinc-blende and wurtzite crystal structures, where no difference is resolvable.[12,18] The calculational uncertainty was estimated by doing two calculations with different relative sphere sizes for ZnS and ZnTe.[19] A somewhat larger uncertainty has been assigned to the ZnO calculation due to the different crystal structure.

In all the Zn chalcogenides roughly equal numbers of s and p electrons are found around Zn, and the variation in electron contact density reflects the increased depletion of charge away from the Zn nucleus with increased electronegativity of the ligand.

Finally, the validity of the frozen-core approximation was tested for Sn and Zn, for which we have performed atomic calculations with different valence configurations. Thus, considering all atomic configurations of Sn, $5s^{n_s}5p^{n_p}$ with $n_s + n_p \geq 2$ we have found that the core contribution to the contact density varies within a range of 1.7 a.u. This should be compared to the interval of $\sim$45 a.u. over which the valence contribution varies for the crystals considered in Fig. 2. At the present level of accuracy the frozen-core approximation thus is reasonable. In fact, it is only in cases of significant ionicity, say for Sn^{3+} and Sn^{4+} ions, that a slight contraction of the core is observed leading to an increase in the core contribution to the contact density, though this never exceeds 5.5 a.u. relative to the $5s^2 5p^2$ atomic ground-state configuration. However, not even for the most ionic compound considered in this work, SnO_2, is an effective charge transfer larger than two away from the Sn atom observed. Similar conclusions have been drawn for Zn.

To summarize the present work, we have demonstrated that it is possible to calculate with good accuracy the valence-electron contact density of a Mössbauer nucleus when it is embedded in its proper solid-state environment. This has facilitated parameter-free calibrations of the ^{119}Sn, ^{121}Sb, and ^{67}Zn isotopes. At the same time we have performed a strong test of the LMTO calculational scheme—somewhat complementary to the usual tests on one-electron energies and structural predictions—because we have applied it to many different types of chemical binding and crystal structures and find that it reproduces the linearity of Eq. (1) exceedingly well. The LMTO method is only slightly more complicated to implement on a digital computer than atomic-structure programs, and it is the feeling of the authors that this, or a similar first-principles solid-state calculational scheme, is far more appropriate for the interpretation of Mössbauer experiments. A detailed discussion of the calculations performed will be published elsewhere.

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[1] For a general review on Mössbauer spectroscopy, see *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978).

[2] B. D. Dunlap and G. M. Kalvius, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), Chap. 2.

[3] G. K. Shenoy and B. D. Dunlap, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), Appendix IV.

[4] T. C. Tucker, L. D. Roberts, C. W. Nestor, T. A. Carlson, and F. B. Malik, Phys. Rev. **178**, 998 (1969).

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[8] I.e., no nucleus at the center, cf. J. Keller, J. Phys. C **4**, L85 (1971).

[9] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[10] Experimental data on ^{119}Sn and ^{121}Sb isomer shifts are averages of the published experimental results, with the 1983 reference scale [J. G. Stevens, Hyperfine Interact. **13**, 221 (1983)] as the primary reference. The ^{67}Zn experimental data are from Ref. 12.

[11] See, e.g., the compilations of previous values for ^{119}Sn and ^{121}Sb in R. L. Ruby and G. K. Shenoy, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), Chap. 9.

[12] G. M. Forster, W. Potzel, and G. M. Kalvius, Z. Phys. B **37**, 209 (1980).

[13] R. A. Pruitt, S. W. Marshall, and C. M. O'Donnell, Phys. Rev. B **2**, 2383 (1970).

[14] H. Z. Dokuzoguz, L. H. Bowen, and H. H. Stadelmeier, Solid State Commun. **8**, 259 (1970).

[15] The effective configuration of a Sn atom in α-Sn is not so easily extracted, since empty spheres are introduced in the interstitial regions. The calculated occupancies inside a Sn sphere of radius 3.02 a.u. are $(n_s,n_p,n_d)=(1.41,1.77,0.13)$ and the remaining 0.69 electrons are in the empty sphere (of the same radius).

[16] R. M. Friedman, R. E. Watson, J. Hudis, and M. L. Perlman, Phys. Rev. B **8**, 3569 (1973).

[17] See T. Katila and K. Riski, Hyperfine Interact. **13**, 119 (1983), for a review on ^{67}Zn Mössbauer spectroscopy.

[18] D. Griesinger, R. V. Pound, and W. Vetterling, Phys. Rev. B **15**, 3291 (1977).

[19] Using equally large spheres around all constituent atoms and using a fixed Zn sphere of radius 2.64 a.u. with the ligand sphere corresponding larger or smaller, respectively.