However, all such effects are included in Pippard's fitting parameter K_{ij}, where

$$\Delta \mathbf{k}_F = \mathbf{n}\epsilon_{ij} K_{ij}(\mathbf{k}_F), \tag{6}$$

and $\mathbf{n}$ is a unit vector perpendicular to the Fermi surface. One could calculate K_{ij} from first principles along the lines suggested by Kleinman in his appendix, or one might measure it with the de Haas–van Alphen effect in crystals with known strains.

Kleinman has suggested a model for studying deformation-potential effects when the actual deformation potential is not known. He makes use of parameters which may be available from experiments or ordinary band calculations, $\mathbf{k}_F$ and $\mathbf{v}_F$, and retains only the first term on the right-hand side of Eq. (1). With Pippard, he considers the excited electron to be at B^P with energy $(\partial E/\partial \mathbf{k})\cdot\Delta\mathbf{k}$. However, instead of treating the Fermi-surface shift as an unknown parameter, he computes it from Eq. (2). Since the second term vanishes for the FED model, he finds

$$\Delta E_F{}^{\mathrm{FED}} = \langle (\partial E/\partial \mathbf{k})\cdot \Delta \mathbf{k}\rangle_{\mathrm{FS}}, \tag{7}$$

indicated by C^F in Fig. 1.

Using (1), (2), and (7) we find that the error which results from the FED approximation is

$$\Delta E - \Delta E^{\mathrm{FED}} = \Delta E_{BS}(\mathbf{k}_F) - \langle \Delta E_{BS}\rangle_{\mathrm{FS}}. \tag{8}$$

In this case of metals for which $\mathbf{k}_F$ and $\mathbf{v}_F$ are known, one could study discrepancies between measured attenuation and that calculated using the FED model to learn the relative importance of the error described by Eq. (8) for the electrons which dominate the attenuation.

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Interpretation of the Mössbauer Isomer Shift in ^{119}Sn†

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The determination by the internal-conversion method of the fractional charge-radius change $\delta R/R$ for the 23.9-keV $M1$ transition in ^{119}Sn is reexamined. A modified $\delta R/R$ value is obtained; this is compared with values otherwise determined, and some implications of these comparisons are derived.

In a letter[1] on chemical effects on valence-electron internal conversion of the 23.9-keV magnetic dipole transition in ^{119}Sn, and on interpretation of the Mössbauer isomer shift for that transition, it was reported that the ratio of O-shell-to-N_1-shell conversion is (0.108 ± 0.004) when the source is in the form of white tin metal and (0.074 ± 0.004) when in the form SnO_2. The derivation from these experimental results of the change in charge radius of ^{119}Sn upon excitation needs modifications which produce effects on the magnitude of $\delta R/R$ but not on its sign. After rederiving the result for $\delta R/R$, we comment on the results implied for the internal-conversion experiment by other interpretations of the isomer shift.

First, an error was made in Ref. 1 in the values of s electron density at the nucleus.[2] From the results of the Hartree-Fock-Slater calculations of Herman and Skillman,[3] we find the nonrelativistic electron density at the nucleus for the two $4s$ electrons to be

$$|\Psi_{4s}(0)|^2 = 320.8 a_0^{-3}.$$

The experimental results[1] then imply that between β-Sn and SnO_2 the change in valence electron density (equivalent nonrelativistic density) at the nucleus is

$$(|\psi_{5s}(0)|_{\beta\text{-Sn}}{}^2 - |\psi_{5s}(0)|_{\mathrm{SnO_2}}{}^2) = (10.9\pm1.8) a_0^{-3},$$

where the uncertainty shown is due to the experimental uncertainty and does not include any contribution from

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[1] J.-P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, Phys. Rev. Letters **17**, 809 (1966).

[2] For which the present authors were responsible. We wish to thank Dr. F. Pleiter and Dr. Hans Postma for calling to our attention the possibility of such an error.

[3] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

uncertainty in $|\Psi_{4s}(0)|^2$. This value for the change in valence electron density is about 50% higher than that used in Ref. 1.

Second, a correction was made in Ref. 1 for an expected small increase in density at the nucleus of inner-shell s electrons when the density at the nucleus of valence s electrons decreases.[4] This "monopole shielding effect" was estimated, with the use of nonrelativistic self-consistent-field results, to give

$$\Delta\left(\sum_{n=1}^{5}|\psi_{ns}(0)|^2\right)=0.84\Delta|\psi_{5s}(0)|^2.$$

An examination of the results of relativistic self-consistent-field calculations[5,6] shows that a much smaller correction, whose sign is uncertain, is probably more appropriate. It turns out that the nonproportionality between $\Delta|\Psi(0)|^2$ and $5s$ electron number arises almost entirely from adjustments in the $5s$ wave function. The inner-shell wave functions change very little, and the $5s$ effects are included in the internal-conversion measurements. We now conclude that the factor 0.84 should be changed to 1.00 with an uncertainty which would appear, from Refs. 5 and 6, to be about 4%.

A value for $\delta R/R$ can then be found by using the relativistic correction factor $S'(Z=50)=2.31$ as given by Shirley,[7] and the measured isomer shift of Lees and Flinn,[6] $v=2.48\pm0.03$ mm/sec. In this way

$$\delta R/R=(1.84\pm0.37)\times10^{-4},$$

where the uncertainty is found by compounding quadratically the experimental uncertainty, the assumed 4% uncertainty in the "monopole shielding factor," and an assumed 10% uncertainty in the product $S'|\Psi_{4s}(0)|^2$. This value then supersedes the value, 3.3×10^{-4}, given in Ref. 1. If we had used the value for $|\Psi_{4s}(0)|^2$ given by Lees and Flinn,[6] we would have found $\delta R/R=(1.73\pm0.35)\times10^{-4}$, less than 10% smaller. Hafemeister[8] has shown that different approximate ways of including exchange in self-consistent-field calculations can lead to considerable differences in results for valence electron density at the nucleus, but that the differences are not so large for inner shells. The calculated L- and M-shell conversion coefficients of Hager and Seltzer,[9] found with wave functions from a relativistic self-consistent-field procedure with modified Slater exchange, are in very good agreement with the experimental total conversion coefficient of Kostroun and Crasemann[10] (and the earlier value of Benczer-Koller[11]), and with the shell and subshell ratios reported previously.[12]

Finally, it should be remarked that the experiment of Ref. 1 yields not only differences in valence electron density relative to the $4s$ density at the nucleus, but gives a relative density value for each chemical form investigated. The equivalent nonrelativistic $5s$ densities determined from the data, using the same $4s$ normalization as was used to determine $\delta R/R$, are $|\Psi_{5s}(0)|_{\beta-\mathrm{Sn}}{}^2=35a_0^{-3}$ and $|\Psi_{5s}(0)|_{\mathrm{SnO}_2}{}^2=24a_0^{-3}$. Put another way, an electron-density calibration for the isomer shift should be able to reproduce both of the O/N_1 ratios given in the first paragraph. From the calibration of Lees and Flinn,[6] which gave $\delta R/R=0.92\times10^{-4}$, one would predict the ratios to be 0.073 for β-Sn and 0.013 for SnO_2, about 67 and 18% of the measured values, respectively. In the same way, the calibration of Ruby, Kalvius, Beard, and Snyder,[13] which gave $\delta R/R=(1.2\pm0.4)\times10^{-4}$, leads to the ratios 0.055 for β-Sn and 0.006 for SnO_2, about 51 and 8% of the measured values, respectively. Both these calibrations were based on free-atom models, and it was pointed out by Ruby *et al.* that more complicated molecular or crystalline models may be necessary before a complete understanding of these phenomena is achieved.[13a] Recently, a different "experimental" calibration of the Sn^{119} isomer shift, based on comparison of the temperature dependences of the isomer shift and of the Knight shift in nuclear magnetic resonances, has been made by Rothberg, Guimar, and Benczer-Koller,[14] yielding the value $\delta R/R=(1.8\pm0.4)\times10^{-4}$, in good agreement with the revised result given above.

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