PHYSICAL REVIEW VOLUME 159, NUMBER 2 10 JULY 1967

Interpretation of Mössbauer Measurements in Tin and Antimony*

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(Received 2 September 1966; revised manuscript received 24 February 1967)

Using the Mössbauer effect in Sb^{121}, measurements of the isomeric shift and quadrupole splitting have been made in a variety of antimony compounds. This data, along with similar results in Sn^{119} by earlier authors, have been interpreted using Hartree–Fock self-consistent-field atomic wave functions. New values are: $(\delta r/r)(Sn^{119})=(1.2\pm0.4)\times10^{-4}$, $Q(Sn^{119})=(-0.06\pm0.02)$ b, $(\delta r/r)(Sb^{121})=(-8.5\pm3.0)\times10^{-4}$, and $Q(Sb^{121}\,\frac{5}{2}{+})=(-0.26\pm0.1)$ b. The interpretation for Sn extends the work of Shpinel, Boyle, and Flinn; the result $(\delta r/r)(Sn^{119})>0$ is opposite to a conclusion recently reached by Gol'danskii. The value for $(\delta r/r)(Sb^{121})$ is much larger than that anticipated by a simple nuclear model.

I. INTRODUCTION

SHORTLY after the decay scheme for mass-121 was clarified,[1] it was shown that the 37-keV level in Sb^{121} was suitable for Mössbauer measurements.[2] The next investigation[3] concentrated on a determination of the ratio of the quadrupole moments in the first excited state and ground state, since this nuclear parameter is essential for the accurate determination of isomeric shifts from any subsequent data. One purpose of the present paper is to give results of further measurements on a variety of antimony compounds, and to interpret these results in terms of the electronic configurations of the antimony atom.

Early in the work it was realized that there are several pairs of compounds in which tin and antimony atoms are isoelectronic with each other. Thus, the interpretation used for the well-studied Sn^{119} nucleus could be readily extended to Sb^{121}. Unfortunately, some disagreement still exists on the interpretation of the Sn^{119} data. As will be discussed below, most authors[4–7] have used an atomic description of the tin electronic wave functions, along with Fermi-Segré calculations of the charge density at the nucleus; these results can be briefly summarized by giving

$$(\delta r/r)(Sn^{119})\cong+1.5\times10^{-4}$$

for the fractional change in nuclear charge radius. However, a recent paper,[8] using molecular orbital theory along with Fermi-Segré calculations, has interpreted the isomeric shifts in the tin tetrahalides such that $(\delta r/r)(Sn^{119})<0$. Here we shall continue to use the atomic description; however, Hartree–Fock self-consistent-field (SCF) computations are now used to provide values of $|\psi(0)|^2$ and $\langle r^{-3}\rangle$ for both Sn and Sb. Another purpose of this paper is to give improved values for $\delta r/r$ and Q for Sn^{119}.

One quantity can be obtained from our data which is nearly independent of the chemical controversy mentioned above. This is the ratio of the fractional changes in nuclear mean charge radius for Sn^{119} and Sb^{121}. The only requirement is that one compare isoelectronic compounds (and make a fairly straightforward correction for the different effective Z). Similar ratios have previously been found (a) between different isotopes of the same element, as illustrated[9] by I^{127} and I^{129} or by[10] Eu^{151} and Eu^{153}, or (b) between different levels of the same nucleus, as illustrated[11] by the 97.5- and 103.2-keV levels in Eu^{153}. Such ratios are expected to be quite useful in testing nuclear models.

II. EXPERIMENTAL PROCEDURE

The valence of antimony is usually three or five. Most of the compounds studied have noncubic symmetry at the antimony site, and consequently an

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* Work performed under the auspices of the U. S. Atomic Energy Commission and the National Science Foundation.

[1] Y. Y. Chu, O. C. Kistner, A. C. Li, S. Monaro, and M. L. Perlman, Phys. Rev. **133**, 1361 (1964); R. L. Auble, W. H. Kelley, and H. H. Bolotin, Nucl. Phys. **58**, 337 (1964).

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[3] S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, Phys. Rev. **148**, 176 (1966).

[4] V. S. Shpinel, V. A. Bryukhanov, and N. N. Delyagin, Zh. Eksperim. i Teor. Fiz. **41**, 1767 (1961) [English transl.: Soviet Phys.—JETP **14**, 1256 (1962)].

[5] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Proc. Phys. Soc. (London) **79**, 416 (1962); O. C. Kistner, V. Jaccarino, and L. R. Walker, in *Proceedings of the Second International Conference on the Mössbauer Effect, Saclay, France, 1961*, edited by H. Schoen and D. M. J. Compton (John Wiley & Sons, Inc., New York, 1962), p. 264.

[6] J. Lees and P. A. Flinn, Phys. Letters **19**, 186 (1965).

[7] V. I. Gol'danskii, G. M. Goradinskii, S. V. Karyagin, L. A. Korytko, L. M. Krizhanskii, E. F. Makorov, I. P. Suzdolev, and U. V. Khrapov, Dokl. Akad. Nauk SSSR **147**, 127 (1962).

[8] I. B. Bersuker, V. I. Gol'danskii, and E. F. Makarov, Zh. Eksperim. i Teor. Fiz. **49**, 699 (1965) [English transl.: Soviet Phys.—JETP **22**, 485 (1966)].

[9] G. J. Perlow and S. L. Ruby, Phys. Letters **13**, 198 (1964).

[10] U. Atzmony and S. Ofer, Phys. Letters **14**, 284 (1965); E. Steichele, S. Hüfner, and P. Kienle, *ibid.* **21**, 220 (1966).

[11] E. Steichele, S. Hüfner, and P. Kienle, Phys. Rev. Letters **14**, 321 (1965).

TABLE I. Experimental results from Mössbauer measurements of the quadrupole splitting and the isomeric shift for some tin and antimony compounds.

Antimony compounds				Tin compounds		
Quadrupole splitting[a] $\frac{1}{4}eQV_{zz}$ (mm/sec)	Isomer shifts[a] relative to InSb (mm/sec)	Compound	Configuration of valence electrons	Compound	Isomer shifts[b] relative to α-tin (mm/sec)	Quadrupole splitting[b] $\frac{1}{4}eQV_{zz}$ (mm/sec)
[0][c]	(+12.3)[d]	(Sb^{5+})	$5s^0p^0$	(Sn^{4+})	(−2.04)[b]	[0]
+2.0±0.4	+12.3±0.4	$KSbF_6$		K_2SnF_6	−2.17	
		SbF_5		SnF_4	−1.92	0.85
−2.1±0.2	+9.9±0.2	Sb_2O_5		SnO_2	−1.75	0.2±0.1
0.0±0.2	[0]	InSb	$5sp^3$	α-tin	[0]	0
	−2.66+0.1	Sb in β-tin		β-tin	+0.66	0.15±0.1
+4.7±0.1	−3.02±0.05	Sb_2O_3		SnO	+0.91±0.1	0.67±0.01
+4.9±0.2	−6.0±0.2	SbF_3		SnF_2	+1.65±0.02	0.80±0.01
[0]	(−16.6)[d]	(Sb^{3+})	$5s^2p^0$	(Sn^{2+})	(+3.02)	[0]

[a] This investigation.

[b] P. Flinn (private communication); A. J. F. Boyle *et al.*, Ref. 5.

[c] Values in square brackets are assumed.

[d] Values in round parentheses are calculated by the method explained in the text.

electric field gradient at the nucleus. The resulting eight-line nuclear quadrupole spectra (the spins are $\frac{7}{2}+$ for the first excited state and $\frac{5}{2}+$ for the ground state) are only poorly resolved because the nuclear lifetime is rather short ($T_{1/2}=3.5\times10^{-9}$ sec). Figure 1 shows two typical spectra; the bar diagrams illustrate how they are analyzed to extract the quadrupole-splitting parameter $eQV_{zz}=eQd^2V/dZ^2$ and the isomer shift S.

The results quoted here (see Table I) for eQV_{zz} refer only to the ground ($\frac{5}{2}+$) state of the antimony nucleus. As discussed in Ref. 3, the value of the quadrupole moment for the excited ($\frac{7}{2}+$) state is not completely unambiguous; however, that uncertainty does not affect any conclusions made in this paper.

The experimental arrangement is the same as in Ref. 3. All measurements reported have been made at 4.2°K by use of a glass cryostat and an electromechanical drive. The motion was sinusoidal and phase locked to a 400-channel multiscaler. The source is antimony in white tin.[2] However, the isomer shifts reported here are all given as if the source had been InSb at 4.2°K.

A velocity of approach is taken as positive. The various absorbers were prepared by grinding the appropriate compound (the amount used corresponded to about 6 mg/cm² of natural antimony) with Lucite and pressing it into a solid disk. Our experimental results are given in Table I.

III. DISCUSSION

To understand the antimony shifts in terms of electronic structure, we have placed considerable stress on its chemical similarity with tin which is (1) its neighbor in the periodic table, and (2) a very well studied Mössbauer nucleus. Our basic procedure is to identify two chemical compounds as corresponding to two definite electronic states. Then it is necessary to obtain the appropriate difference in $\psi^2(0)$ for these states. The electronic charge density at the nucleus and $\langle a_0^3/r^3\rangle$ for the $5p$ electrons have been found by a Hartree-Fock self-consistent-field computation[12] (a_0 is the Bohr radius). These computations will be discussed further below. The results are listed in Table II; in part they are also displayed in Figs. 2 and 3. These

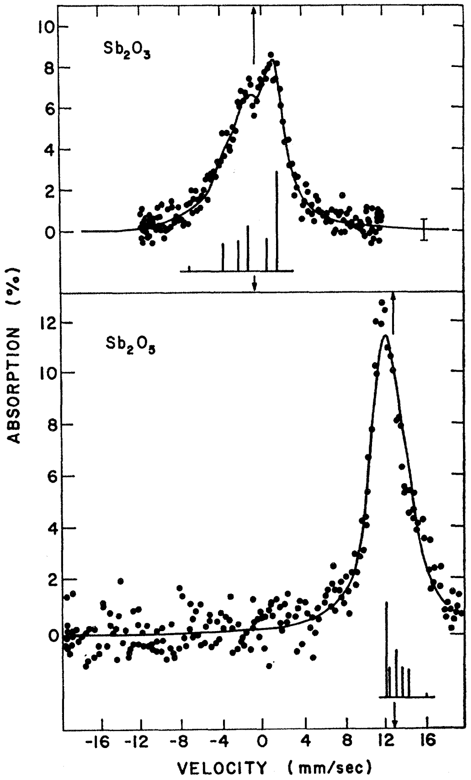

FIG. 1. Mössbauer spectra of Sb_2O_3 and Sb_2O_5. Both spectra show unresolved quadrupole splitting. The solid curve is a least-squares fit reached by a computer technique described in Ref. 3. The position of the hyperfine lines is given as a bar diagram, and the isomer shifts are marked by arrows.

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[12] The calculations were performed by Dr. Michael Wilson of the Argonne National Laboratory by use of computer program originally developed by Dr. Charlotte Frouse of the University of British Columbia.

TABLE II. Values of the electron density at the nucleus and the inverse cube radius of the $5p$ electrons (in units of the Bohr radius a_0) for different electronic configurations of tin and antimony, as computed. The number $K=93\,291$ is the contribution of the closed inner shells on antimony. The corresponding number for tin is $K=87\,919$.

Atomic state	Electron configuration	$[\psi^2(0)/a_0^3]-K$	$\langle a_0^3/r^3\rangle_{5p}$	$\Delta\psi^2(0)_{\mathrm{Sb}}/\Delta\psi^2(0)_{\mathrm{Sn}}$
Sb I	$5s^25p^3$	26.72	9.23	1.36
(Sn$^-$)		19.65	5.01	
Sb II	$5s^25p^3$	36.22	11.10	1.36
Sn I		26.84	6.75	
Sb III	$5s^25p$	40.55	13.05	1.36
Sn II		29.85	8.54	
Sb IV	$5s^2$	44.45	...	1.32
Sn III		33.62	...	
Sb II	$5s5p^3$	18.28	11.14	1.34
Sn I		13.62	6.91	
Sb III	$5s5p^2$	19.97	13.02	1.33
Sn II		15.01	8.60	
Sb IV	$5s5p$	22.10	14.99	1.31
Sn III		16.89	10.40	
Sb V	$5s$	24.59	...	1.29
Sn IV		19.07	...	
...	$5s^05p^0$	0	...	...
		0		
	$5s^05p$	...	...	
		−0.44	...	
	$5s^05p^2$	...	...	
		−0.70	...	
	$5s^05p^3$	...	...	
		0.80	...	

graphs reinforce ones qualitative feelings. For example, the charge density increases nearly linearly with the number of $5s$ electrons; the effect of self-shielding is evident in the sign of the nonlinearity; and the effect of adding $5p$ electrons is to decrease the charge density by increasing the shielding.

As outlined by Shirley,[13] the isomer shift is given by the expression

$$S=(c/E_\gamma)F(Z)\Delta\psi^2\delta r/r, \tag{1}$$

where $F(Z)$ was defined as

$$F(Z)=\tfrac{4}{5}(\pi Ze^2R^2)S'(Z). \tag{2}$$

Here $S'(Z)$ is the relativity factor which has to be included if ψ^2 is found by a nonrelativistic calculation. This factor $S'(Z)$ is introduced to transform the nonrelativistic, and therefore uncorrect, ψ^2 to an electron density which would have been found by a proper relativistic calculation. The major part of $S'(Z)$ is contributed by the well-known enhancement of ψ^2 found by Racah in the solution of the Dirac equation for a single electron moving in a point-charge Coulombic field. This, and further modifications to include the finite nuclear size, as well as numerical tables, are all given in Shirley's useful article.

An associated question of considerable importance is how to handle the relativistic self-consistent-field problem. One approach is to include the relativistic effects from the beginning, use a Dirac Hamiltonian and then construct a Hartree-Fock program on this. This is a formidable undertaking; however, useful results are emerging from the efforts of Dr. Liberman and others at Los Alamos Scientific Laboratory. Another approach is to decide how nearly the enhancement factor computed for a single electron will also apply to each and all of the electrons in the self-consistent-field problem. That this direction is plausible is suggested by the fact that the enhancement factor computed by Racah for s electrons does not contain parameters reflecting the electron energy. A virtue of this approach is that it allows the continued use of the present sophisticated nonrelativistic SCF programs even for atoms of rather high Z.

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[13] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).

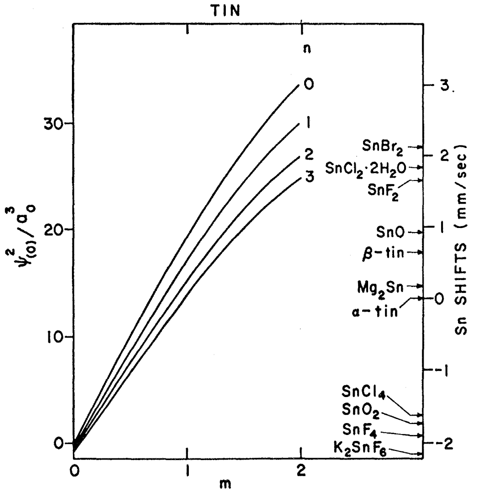

FIG. 2. Correlation between electron density $\psi^2(0)/a_0^3$ at the nucleus and the isomer shift for Sn^{119} as a function of the number m of 5s electrons. The parameter n is the number of 5p electrons. The experimental points are from Refs. 5 and 6.

The second approach, which is essentially that suggested by Shirley, has been continued in this paper. As support for the correctness of this view, there is a recent paper by Hafemeister[14] in which he makes a detailed comparison between the Los Alamos relativistic SCF programs, the nonrelativistic but otherwise more elaborate SCF programs such as that used here, and the Racah correction factor as shown in Ref. 3. His conclusion is that for s electrons at the present stage the second approach is quite satisfactory. For $p_{1/2}$ electrons though, the nonrelativistic approach fails completely to account for their nonzero density at the nucleus. However, numerical results are presented from the relativistic SCF programs showing that the $5p_{1/2}$ density is only about one electron per atomic volume. This $5p_{1/2}\ \psi^2(0)$, which is only about 2% of the relativistic $5s\ \psi^2(0)$, is not large enough to change Figs. 2 and 4 in more than detail. Its main effect is in the direction opposite to the shielding also caused by the p electrons, and their result would be to draw the four lines of Figs. 2 and 4 somewhat closer together. The values given for ψ^2 in Table II and in Figs. 2 and 3, are nonrelativistic results, and have not been corrected by the relativistic factor, nor adjusted for $p_{1/2}$ contributions.

Now we shall combine the experimental results on tin with our new Hartree-Fock computations in order to improve the nuclear parameters and to provide a uniform basis for the comparison of the antimony measurements. Our interpretation for the isomer shifts in tin is based on the paper of Lees and Flinn,[6] who correlate measurements on eQV_{zz} and S for a large number of Sn^{2+} compounds. Their results quantitatively support the earlier interpretation[5] based solely on the isomer shifts. In common with the other authors, Lees and Flinn identify grey tin with the electron configurations $5s5p^3$. Their second point of reference is the configuration $5s^25p^0$ whose shift, obtained by extrapolating the isomer shifts of stannous compounds to zero quadrupole splitting, is +3.02 mm/sec from that of α-tin. This differs noticeably from earlier work in which the shift measured in SnF_2 was assigned to $5s^25p^0$. From Table II, we find that the difference $\Delta\psi^2$ between $5s5p^3$ and $5s^25p^0$ is $20.0/a_0^3$. Using Eq. (1) with $F(50)=(1.04\times10^{-4}\ \text{eV}\times a_0^3$, one finds that the fractional change in the charge radius of Sn is $\delta r/r=1.2\times10^{-4}$. This may be compared with the earlier result of Boyle *et al.*[5] who gave 1.1×10^{-4}, and also Gol'danskii,[7] who gave 1.9×10^{-4}. In addition, a recent theoretical calculation,[15] using a pairing-plus-quadrupole model for the nucleus, has predicted $\delta r/r(\text{Sn}^{119})=0.75\times10^{-4}$.

It is now possible to predict the isomer shift for any other configuration. In particular, it can be seen from Fig. 2 that any configuration $5s^05p^n$ without s character, regardless of the number of p electrons, will have a shift of about −2.1 mm/sec.[16] It would be anticipated that the closest approach to this configuration is made by surrounding the tin atom as closely as possible with the most electropositive atoms, and indeed the compounds SnF_4 and K_2SnF_6 do possess shifts of just this size. The agreement between these shifts and the value computed for $5s^0p^n$ is a strong argument for the correctness of the calculated wave functions and the atomic interpretation.

In Fig. 2 the isomer shifts of various compounds are labeled along the right-hand ordinate. It is to be noted that a range of configurations is compatible with each isomer shift. Utilization of the quadrupole splitting

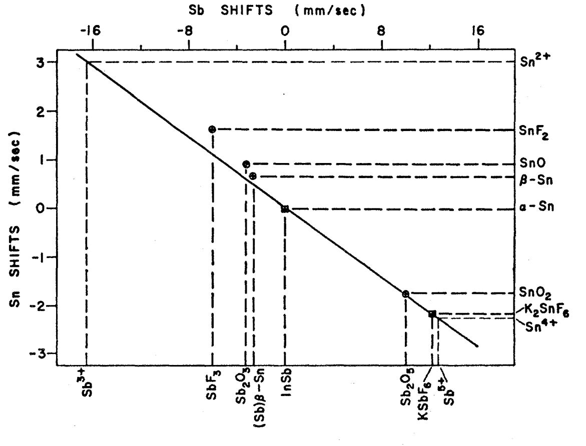

FIG. 3. Relation between the isomer shifts of similar compounds of tin and antimony. The two points marked by squares are used to generate the straight line. The pairings $\text{Sn}^{2+}:\text{Sb}^{3+}$ and $\text{Sn}^{4+}:\text{Sb}^{5+}$ are calculated as explained in the text.

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[14] D. W. Hafemeister (to be published), now at Carnegie Institute of Technology, Pittsburgh.

[15] R. A. Uher and R. A. Sorensen, Nucl. Phys. **86**, 1 (1966) and private communication.

[16] P. A. Flinn, who used relativistic wave functions, has informed us he also gets this result.

measured in the same compound can decrease this ambiguity since the quadrupole splitting can be proportional to the number of p electrons. The numerical proportionality between the isomer shift and the quadrupole splitting for stannous compounds[6] is that one p_z electron produces $\frac{1}{2}eQV_{zz}=2.97$ mm/sec. Using $\langle a_0^3/r^3\rangle=10.4$ for the configuration $5s5p$ from Table II, the quadrupole moment is found to be $Q=-0.06$ b. This value is preferable to the older -0.08 ± 0.04 which was obtained[17] with the value of $\langle r^{-3}\rangle$ appropriate to $5s^2p^3$. No correction for the Sternheimer antishielding factor has been made.

Turning now from tin to antimony, the above interpretation for the isomer shifts can be employed again for any compounds in which the antimony atom is isoelectronic with an interpreted tin configuration. We begin by assuming that InSb is isoelectronic with α-tin, since the compounds are similar in most respects. That InSb also involves sp^3 hybridization is evident by its tetrahedral diamondlike lattice. For a second calibration point, we assume that $KSbF_6$ is isoelectronic with K_2SnF_6. With these two points and the computed values for ψ^2, the isomeric shift for any other antimony configuration can be calculated. Table I lists such values for Sb^{5+} and Sb^{3+}. In Fig. 3, in which isomeric shifts in analogous compounds of Sb and Sn are plotted against each other, the solid line is drawn through these points. If indeed the metal ions are isoelectronic within each of the pairs (α-tin, InSb) and (K_2SnF_6, $KSbF_6$), then any other isoelectronic pairs will also lie on this solid line. This fact will be used to test our assumptions.

It is anticipated that an antimony impurity atom in β-tin will operate as a donor, the extra electron will be lost in the conduction band, and the remaining atomic electrons will be nearly indistinguishable from those on an ordinary tin atom, except for the influence of the higher effective Z. Thus our source (antimony in β-tin) is expected to form an isoelectronic pair with the tin atom in β-tin. The remaining pairings shown in Table I are suggested by a naive ionic model; as an example, both SnF_2 and SbF_3 would have the configuration $5s^25p^0$ if the most weakly bound electrons are simply transferred to the fluorine atoms. Things are not actually that simple, of course, as is shown here by the fact that both compounds exhibit substantial quadrupole splitting and therefore possess considerable $5p$ character. For our purpose of transferring configurations from tin to antimony, a pairing is satisfactory if the same description $5s^mp^n$ applies to both. The fact that $m+n\approx2$ for divalent tin compounds, which is implicit in the results of Lees and Flinn,[6] will be useful later when discussing quadrupole moments.

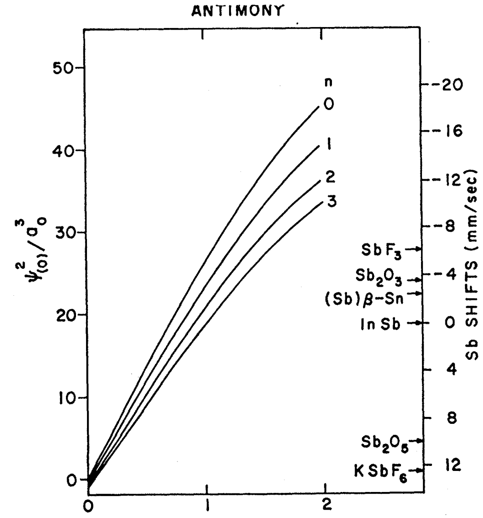

FIG. 4. Same correlation of electron density at the nucleus and isomer shift as in Fig. 2, but for Sb^{121}. The experimental points are from this investigation.

Our interpretation of Fig. 3 is that the lower four points represent nearly isoelectronic pairs. This implies that the atomic configuration $KSbF_6$ is approximately $5s^05p^n$, a fact we shall use below. The deviations from the line of the other two points are easily interpreted as resulting from the dissimilar crystal structures changing the relative amounts of s and p bonding; only if these compounds were ionic, would it be likely for them to form isoelectronic pairs. It should be emphasized that measurements of isomeric shifts can be sensitive to small changes in electronic configuration. In the present case, for example, the (α-tin, InSb) point would be raised in the diagram so that the solid line would pass exactly through the [β-tin, (Sb) β-tin] point if the effective value of m for antimony was taken to be 0.97 rather than the 1.0 assumed. Having now shown that our assumptions about isoelectronic configurations are justified, we can proceed to plot (Fig. 4) the isomeric shift versus configuration for Sb. As before, for an unambiguous determination of the electronic state, separate information on the number of p electrons is required.

From Fig. 3, the slope of the solid line is found to be -5.4 to which we rather arbitrarily assign an error of 20%. From Eq. (1), this ratio must satisfy the relation

$$-5.4(1\pm0.20)=\frac{23.8}{37.2}\frac{\Delta\psi_{\mathrm{Sb}}^2}{\Delta\psi_{\mathrm{Sn}}^2}\frac{(\delta r/r)_{\mathrm{Sb}}}{(\delta r/r)_{\mathrm{Sn}}}\frac{F(51)}{F(50)}. \quad (3)$$

The Hartree-Fock calculations show that $\Delta\psi_{\mathrm{Sb}}^2/\Delta\psi_{\mathrm{Sn}}^2=1.33\pm0.03$, and $F(51)\ F(50)=1.04$, therefore the ratio of the fractional changes in radius becomes -6.1 ± 1.5. It is believed that this new method of comparing changes in nuclear radii can be extended to other pairs of isotopes, especially in the sequence from Sn to Cs.

The fractional change in charge radius $(\delta r/r)_{\mathrm{Sb}}$ can also be found directly. We begin by assuming that K_2SnF_6 has the configuration $5s^0p^3$, and that InSb corresponds to $5s5p^3$. From Table II, we estimate

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[17] R. G. Barnes and W. V. Smith, Phys. Rev. 93, 95 (1954).

$\Delta\psi^2=19.3a_0{}^3$. The measured isomer shift is 12.3 mm/sec, and from Ref. 13, we take $F(51)=(1.085\times10^{-4}\text{ eV})a_0{}^3$. Equation (1) then gives $(\delta r/r)_{\text{Sb}}=-8.5\times10^{-4}$.

This can be compared with the calculations of Uher and Sorensen[15] who give $+0.08\times10^{-4}$. The reason for the inadequacy of their model for Sb^{121} is not understood, in view of its "factor-of-2" success for Fe^{57}, Kr^{83}, and Sn^{119}. It seems clear that the fractional change in mean charge radius is a delicate nuclear property and will provide an exacting test for nuclear theory.

Further, a rough estimate of $Q_{\text{Sb}}(\frac{5}{2}+)$ can now be made using eQV_{zz} for SbF_3 and Sb_2O_3. The quadrupole splitting parameter can be equated to the product of the unknown nuclear quadrupole moment and the field gradient produced by the unknown number n of p_z electrons. However, the isomer shift enables us to make a fairly good estimate for m, the effective number of s electrons. Then, assuming $m+n=2$, as is the case for divalent tin we get n and therefore Q. For one $5s5p$ electron Table II gives $\langle a_0/r^3\rangle=14.99$; then, $eQV_{zz}=-\frac{4}{5}e^2Q\langle r^{-3}\rangle=Q(1134\times10^{-8})$ eV. Using $m=1.25$ (see Fig. 4) and $eQV_{zz}=243\times10^{-8}$ eV for SbF_3 (merely applying a conversion factor to a number given in Table I) we find $Q=-0.29$ b. Similarly, for Sb_2O_3 with $m=1.1$ and $eQV_{zz}=228\times10^{-8}$ eV, $Q=-0.23$ b. Again shielding corrections have not been made. It should be remarked that the inner shielding involved here does not give rise to large effects. A recent paper[18] on electric field gradients in Sb metal concludes that this effect increases the field at the nucleus by only 10%, and this would lead to a corresponding reduction of the moments.

The confidence that can be placed in these numbers should be somewhat limited in view of the several uncertain assumptions involved in their derivation. However, they may be compared with the recently published[19] value $Q^{121}(\frac{5}{2})=-0.29$ b, which was derived as a weighted average of the experimental results -1.3, -0.50, -0.54, and -0.20 b, obtained by optical spectroscopy and atomic-beam techniques.[20–23] In addition there are two theoretical estimates of this quantity, namely -0.43 b by Kisslinger and Sorensen[24] and -0.26 b by Horie and Arima.[25] It appears safe to accept for now a value $Q^{121}(\frac{5}{2})=-0.28\pm0.1$ b.

IV. CONCLUSIONS

Antimony compounds in which the antimony atoms are believed to be isoelectronic to tin atoms in analogous compounds have been measured to allow comparisons of their isomer shifts for Sn and Sb. In this way, the unexpected result has been found that $\delta r/r$ for Sb^{121} is between 6 and 7 times larger than for Sn^{119}, and of opposite sign.

Using Hartree-Fock SCF atomic calculations, the Mössbauer data on Sn^{119} compounds have been reevaluated. The interpretation predicts a shift of about -2.1 mm/sec for Sn^{4+}; -2.17 is measured for K_2SnF_6. The analysis leads to $(\delta r/r)\ \text{Sn}^{119}=(1.2\pm0.4)\times10^{-4}$, and $Q(\text{Sn}^{119})=(-0.06\pm0.02)$ b. These differ only slightly from earlier values. A similar analysis for Sb^{121} leads to $\delta r/r=(-8.5\pm3)\times10^{-4}$ and $Q(\frac{5}{2}+)=-0.26$ b. The latter result is in agreement with the weighted average of the widely scattered results of other experiments. The results indicate that isomer shifts and quadrupole splittings in these compounds when described together are sensitive to small changes of the electronic configuration. More sophisticated calculations of the electronic structure can be tested with experimental data of this kind.

A remark should be made in reference to the controversy in the interpretation of the tin data. The atomic interpretation is consistent with the whole scale of isomer shifts, while the new molecular orbital analysis[8] concentrates on only three shifts—those for SnCl_4, SnBr_4, and SnI_4. Unfortunately, here even the raw experimental data are subject to considerable uncertainty, in part owing to the difficulty of getting (and keeping) crystallographically good samples of these powders.[26] In addition, these shifts cover only about one-third of the whole range. No suggestion has been given so far as to how to interpret the shifts of the divalent compounds and in particular their relation to the quadrupole splitting if indeed $\delta r/r<0$. The method of correlating the "ionicity" as obtained from EQR data with the isomer shift from Mössbauer experiments as put forward for the tetrahalides in Ref. 8 is an important contribution by itself. The dilemma to which it leads is due to the assumptions one has to make in regard to the s or p character of the electrons transferred to the ligand. As Fig. 2 shows, a removal of p electrons will increase the electron density at the nucleus, while a removal of s electrons will decrease it. Therefore, the evaluation of the sign of $\delta r/r$ will crucially depend on the interpretation of the character of the transferred electrons, in particular, if only a rather small range of shifts (like the tetrahalides) is looked at. A definite answer cannot be given at the present time. It should be stressed that Gol'danskii's correlation between isomer shift and ionic character is *per se* not contradictory to the atomic interpretation

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with $\delta r/r > 0$. For these reasons, we prefer so far the older analysis.[27]

However, work has to be continued along the lines marked out in Ref. 8. The Mössbauer literature, for all isotopes, has been dominated so far by rather primitive "atomic" descriptions; in the long run, better molecular, or crystalline, models must be devised to correlate the various measurements that can be made.

ACKNOWLEDGMENTS

We wish to acknowledge our debt to Dr. Michael Wilson for his considerable help in teaching us about SCF atomic calculations and to Dr. Gordon Goodman for a stimulating conversation with regard to chemical theory. Bruce Zabransky and James Tison made many contributions to this work in the laboratory.

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[27] As this work was in press, an important paper [J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, Phy. Rev. Letters, **17**, (1966) 809] was published which employed new experimental data on conversion electron intensities to deduce $\delta r/r = +3.1\times10^{-4}$. This result is strong support for positive fractional change of the nuclear charge radius. The remaining difference in numerical values can be traced to the following facts: After difficult unfoldings of complex spectra, they found that the conversion rate in the 5*s* shell decreased by 25% in going from β-tin to SnO_2. On the other hand, the analysis given here indicates (see Fig. 2) that a 75% decrease would have been more satisfactory.

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Energy Levels of Yb^{3+} in Gallium and Aluminum Garnets. I. Spectra

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(Received 20 June 1966; revised manuscript received 14 November 1966)

The interpretation of the near infrared spectrum of ytterbium in the gallium and aluminum garnets is greatly simplified by the observation that a majority of the lines can be identified as vibronic by virtue of their symmetric pairing as summation and difference sidebands about the transition connecting the lowest $^2F_{7/2}$ and $^2F_{5/2}$ ytterbium levels. The few lines which cannot be so identified are readily assigned as electronic transitions connecting the remaining $^2F_{7/2}$ and $^2F_{5/2}$ levels. This procedure provides a complete identification of all the 4*f*-electron energy levels of trivalent ytterbium based on experimental evidence alone. It is found that the first excited $^2F_{7/2}$ level occurs above 540 cm^{-1} in the gallium garnets and above 600 cm^{-1} in the aluminum garnets. New assignments are made for the $^2F_{5/2}$ levels in the aluminum garnets, these assignments being more similar to those already made for the gallium garnets. No spectral evidence is found in the gallium garnets for ytterbium ions occupying other than normal sites. However, there is some indication in the aluminum garnets that a small percentage of the ytterbium ions occupy abnormal sites.

INTRODUCTION

THE spectra of ytterbium in the garnets have been reported over the past seven years.[1] It may therefore seem presumptuous and redundant to treat anew the analysis of these spectra. In fact, despite the amount of effort expended, no unambiguous analysis has been achieved prior to this time. That this is so may seem surprising in light of the expected simplicity of the 4*f*-electron energy level scheme of ytterbium. Even taking into account the low (orthorhombic) symmetry of the site on which the rare earths occur in the garnets, only seven levels (three for the $^2F_{5/2}$ and four for the $^2F_{7/2}$ states) are to be expected. The spectrum, consisting of transitions between these two manifolds of levels, would therefore be presumed to be sparse and easily interpreted.

In contrast with expectation, the spectrum is complex. Many more lines than can be explained on the above basis are observed. In the assignments made to date, arbitrary criteria have been used for identifying the few *bona fide* electronic transitions, arbitrary assumptions have been made as to the nature of the crystal field, and certain lines have been discarded without adequate justification. No two sets of prior analyses agree, nor does any agree with the analysis to be presented here.

Ytterbium is one of the few ions for which an exact low-symmetry crystal-field calculation is possible. Ytterbium is furthermore of interest in that it is the one ion for which a reasonable amount of experimental data relating to exchange-field-induced effects in the iron garnets are also available. The exchange-field problem is impossible to pursue in any depth without an adequate solution of the crystal-field problem. In light of the small number of 4*f*-energy levels for ytterbium and the need to use them all in a low-symmetry calculation, the crystal field cannot be obtained without a complete and correct interpretation of the spectrum.

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[1] The majority of the prior studies are summarized by M. T. Hutchings and W. P. Wolf, J. Chem. Phys. **41**, 617 (1964) in connection with their treatment of the crystal-field problem. Certain specific references will be mentioned later in this paper as appropriate.