SOVIET PHYSICS JETP VOLUME 26, NUMBER 5 MAY, 1968

ISOMER CHEMICAL SHIFTS OF THE MOSSBAUER GAMMA LINE IN ISOELECTRONIC ANTIMONY COMPOUNDS

V. A. BRUKHANOV, B. Z. IOFA, V. KOTKHEKAR, S. I. SEMENOV, and V. S. SHPINEL'

Nuclear Physics Institute of the Moscow State University; Moscow State University

Submitted June 23, 1967

Zh. Eksp. Teor. Fiz. 53, 1582–1588 (November, 1967)

We measured the isomer chemical shifts (ICS) of the 37.2-keV γ line of the Sb^{121} nucleus in isoelectronic complex antimony salts $NaSbF_6$, $NaSb(OH)_6$, $HSbCl_6 \cdot \times H_2O$, and also in Sb_2O_3, Sb_2O_5, $SbCl_5$, InSb, and Sb. The $Sn^{121\,m}$ isotope in the β-Sn and SnO_2 lattices was employed as the resonance γ-radiation source. For SnO_2, the emission line of the 37.2-keV resonance γ quanta is singlet and practically unbroadened, whereas the Mössbauer effect (fraction of non-recoil quanta f) at T = 78°K exceeds f for the β-Sn source and equals $f_{78^\circ}(SnO_2) = 0.32^{+0.04}_{-0.02}$. The dependence of the ICS on the electronegativity of the antimony-ligand for six-coordination antimony compounds is found to be linear just as in the case of six-coordination tin compounds of the $SnHal_6^{-2}$ type. By comparing these dependences, a relation is obtained between the relative variations of the mean-square charge radii for two Mössbauer γ transitions (37.2-keV transition in Sb^{121} and 23.8-keV transition in Sn^{119}): $(\delta R/R)_{Sb}/(\delta R/R)_{Sn} = -(5.5 \pm 0.3)$. Calibration of the magnitude of the ICS corresponding to detachment of a 5s electron in the Sb atom is performed by extrapolating the ICS dependence to a completely covalent bond. The value thus found is 29×10^{-7} eV (23 mm/sec). Measurements of the magnitude of the resonance effect as a function of thickness of Sb_2O_5 absorbers yield a value $\alpha \sim 10$ for the total resonance internal conversion coefficient.

We have already shown in [1] that an investigation of the isomer chemical shifts (ICS) of the Mössbauer γ line in isoelectronic compounds of elements with valence electrons in the same shell (in our case—octahedral complex salts of tin and tellurium) makes it possible to relate more reliably the values of the ICS with the singularities of the chemical bond. It turns out to be possible in this case to determine also the relative change of the charge radius in the resonant transition $(\delta R/R)$ for both nuclei, without performing exact calculations of the electron density on the Mössbauer nucleus in a many-electron molecule, which at present cannot be performed with sufficiently high accuracy.

In the present investigation, following the approach developed in [1], we measured the values of the ICS for the 37.2-keV γ line of the Sb^{121} nucleus. Antimony has a valence-shell configuration $5s^25p^3$ and forms a number of octahedral complex salts that are isoelectronic to the tin and tellurium compounds investigated earlier. We report here the results of the measurement of the ICS for these components of antimony and present a comparison of the obtained dependence of ICS on the electronegativity of the ligand with the result of [1].

DESCRIPTION OF EXPERIMENT

The resonant 37.2-keV γ radiation is produced in the decay of the isomer state of Sn^{121m}. (The first communication of the observation of the Mössbauer effect for Sb^{121} nuclei was published in [2].) In our case the resonant sources were made of metallic tin (total weight ~ 500 mg) enriched with Sn^{120} to 98% and activated in a reactor. The irradiated tin was subjected to chemical purification to eliminate the radioactive impurities Sb^{125} and Te^{125m} produced in the reaction $Sn^{124}(n,\gamma)Sn^{125} \rightarrow Sb^{125} \rightarrow Te^{125m}$. The purified tin was used to prepare sources in the form of metallic β-Sn^{121} (electrolysis on a substrate of Au) and in the form of SnO_2.

The resonant γ radiation was recorded with detectors in the form of a photomultiplier FEU-13 with a thin NaI(Tl) crystal (thickness 0.3 mm) and a proportional counter (mixture of xenon and isopentane), using the peak of the 37.2-keV γ-quantum emission. Under the operating conditions, the counting rate in the window of the differential analyzer, set at the emission peak, was on the order of 200–300 counts/sec for the proportional counter and 50–70 counts/sec for the crystal. Comparative measurements of the γ spectra of the sources have shown that the fraction of the useful count κ in the region of the emission peak is appreciably larger in the case of the NaI(Tl) crystal and is close to unity. The measurements were made with both detectors, using an electrodynamic Mössbauer setup operating in the constant-velocity mode.

Since the counting rate turns out to be quite small under the operating conditions, the choice of conditions under which the largest experimental effects would be observed, in order to obtain better statistical accuracy, turned out to be very important. Preliminary measurements were therefore made with both sources, β-Sn^{121} and $Sn^{121}O_2$. It was established that the probability of the Mössbauer effect (the fraction f of recoilless γ quanta for the Sb^{121} nuclei in the SnO_2 lattice is almost twice as large as in the case of the β-Sn matrix. This result is not unexpected if account is taken of the data on the probability of the Mössbauer effect for the 23.8-keV γ transition in the Sn^{119}, according to which the value of f in SnO_2 is much larger than for β-Sn; this can be attributed to the influence of the optical branches of the phonon spectrum.[3]

The width and the emission line shape of the resonance γ quanta from the Sb^{121} in SnO_2 nuclei were veri-

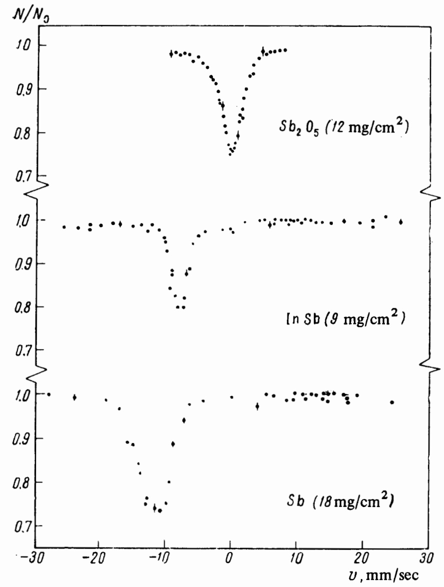

FIG. 1. Examples of resonance-absorption spectra obtained with a $Sn^{121}O_2$ source (measurement temperature 78°K). The absorbers were made of antimony with natural content of the Sb^{121} isotope. The thickness of the absorber is in terms of the Sb^{121} isotope. The abscissas represent the relative velocity in mm/sec, and the ordinates the value of the effect in relative units.

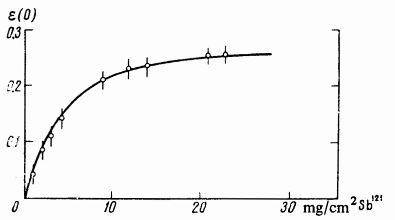

FIG. 2. Dependence of the maximum resonance absorption effect ε(0) on the thickness of the Sb_2O_5 obtained with an $Sn^{121}O_2$ source. The abscissas represent the thickness in mg/cm² in terms of the Sb^{121} isotope. The solid curve is calculated for f = 0.32 under the condition that C = 1 for a thickness 2.8 mg/cm².

fied by measuring the resonance-absorption spectra in the InSb samples. The corresponding spectra were singlet lines of width 2.7–3.0 mm/sec, which made is possible to conclude that there are no mechanisms that broaden noticeably the emission line (natural width $2\Gamma = 2.1$ mm/sec). The spectra of the resonant absorption in Sb_2O_5 were similar (Fig. 1). By way of an example, Fig. 1 shows also the absorption line in the Sb sample, broadened ($\Gamma_{exp} = 6.4$ mm/sec) as a result of the quadrupole interaction.[4]

From the methodological point of view it was of interest to determine the absolute value of f for the Sb^{121} nuclei in the SnO_2 lattice. To this end, we measured the effect ε(0) on Sb_2O_5 samples of different thickness. The measurements were made with a source and absorber at liquid nitrogen temperatures with an NaI(Tl) detector, since it is possible to assume in the calculation of f that $\kappa = 1$ for such a detector. The result of the measurement is shown in Fig. 2.

The dependence of the experimental effect ε(0) on the absorber thickness, as is well known, can be described by the expression (see [5])

$$\varepsilon(0) = \varkappa f[1 - I_0(C/2)e^{-C/2}], \qquad (1)$$

where $C = nf'\sigma_0$, n is the number of the resonant nuclei per cm², f′ is the probability of recoilless absorption of the resonance γ quanta,

$$\sigma_0 = \frac{2I_1+1}{2I_0+1}\frac{\lambda^2}{2\pi}\frac{1}{1+\alpha}$$

(the symbols are standard). Comparison of the experimental and the theoretical dependence of ε(0) on n yields a value $f = 0.32^{+0.04}_{-0.02}$.

We note that the value of f for the 37.2-keV γ transition can be estimated by using data on the Mössbauer-effect probability for the 23.8-keV γ line of Sn^{119} in the SnO_2 lattice. Indeed, we can write

$$f_{SnO_2}(Sn^{119}) = e^{-\mathrm{const}(23.8)^2}, \quad f_{SnO_2}(Sb^{121}) = e^{-\mathrm{const}(37.2)^2},$$

whence, assuming $f_{SnO_2}(Sn^{119}) = 0.65$,[6] we get $f_{SnO_2}(Sb^{121}) = 0.33$.

This value agrees satisfactorily with that obtained by us from the measurements. In addition, this result can be regarded as an indication that the disturbance of the lattice-vibration spectrum, due to the preceding β decay ($Sn^{121} \rightarrow Sb^{121}$), attenuates by the instant of the emission of the resonant quantum and does not affect the value of f.

We also performed measurements with the $Sn^{121}O_2$ source at room temperature. In this case the values of the experimental effects ε(0) were reduced by approximately one-half. Thus, for the $Sn^{121}O_2$ source f amounts to ~0.16 at room temperature.

The dependence shown in Fig. 2 can be used also to estimate the total internal conversion coefficient α for the 37.2-keV γ transition. To this end it is necessary to know the value of f′ for Sb_2O_5. It was noted that f′ for Sb_2O_5 changes by approximately 2–2.5 times on going from nitrogen temperature to room temperature, which is sufficiently close to the situation obtaining in the case of the $Sn^{121}O_2$ source. In addition, the lack of ICS for Sb_2O_5 indicates that the chemical bonds of the antimony atoms with the surrounding oxygen octahedra in Sb_2O_5 and SnO_2 are quite similar. We can therefore conclude that the binding forces of the antimony atoms in the Sb_2O_5 and SnO_2 are also quite close, and consequently, the probability of the effect for Sb_2O_5 is close to that of the case of $Sn^{121}O_5$, that is, ~0.3. Under such an assumption, we obtained from the dependence of ε(0) on the thickness of the Sb_2O_5 absorbers (Fig. 2) a value α ~ 10.

The main measurements of the ICS were made at liquid-nitrogen temperature with an $Sn^{121}O_2$ source. We measured in the spectra of the resonant absorption in Sb_2O_5, Sb_2O_3, $SbCl_5$, $NaSb(OH)_6$, $NaSbF_6$, $HSbCl_6 \cdot xH_2O$, InSb, and Sb. The corresponding absorbers were made of antimony with a natural content of the Sb^{121} isotope. With the exception of Sb_2O_3 and the pure antimony, the resonance-absorption spectra were singlet lines without any noticeable broadening. The values of the experimental effects were not less than 6–7%. The results of the measurements of the ICS are listed in the table.

DISCUSSION OF RESULTS

From among the investigated antimony compounds, direct interest attaches, from the point of view of com-

Values of ICS (δE) for the investigated antimony compounds, obtained with a 37.2-keV γ source in the form of $Sn^{121}O_2$

Compound	ИХС (δE), mm/sec	δE, 10^{-8} eV
$NaSb(OH)_6$	+0.5±0.2	+6,2±2,5
$HSbCl_6 \cdot xH_2O$	−3.0±0.2	−37.2±2.5
$NaSbF_6$	+2.0±0.2	+24.8±2.5
$SbCl_5$	−3.5±0.3	−43.4±3.7
Sb_2O_5	0.0±0.2	0.0±2.5
Sb_2O_3	−10.4±0.3	−127.9±3.7
InSb	−8.4±0.2	−103.3±2.5
Sb (м(metal))	−11.2±0.3	−137,7±3.7

parison with the results of [1], to the complex salts of the pentavalent antimony $NaSbF_6$, $NaSb(OH)_6$, and $HSbCl_6 \cdot xH_2O$. In these complexes, the antimony atoms have an octahedral surrounding, forming equivalent hybrid bonds sp^3d^2 with six ligands (symmetry group O_h^5 [7, 8]). The values of the ICS for the indicated complex antimony salts are shown in Fig. 3 as functions of the difference of the antimony–ligand electronegativity ΔX (the values of ΔX were taken from [9, 10]). The same figure shows the results obtained in the case of octahedral complex salts of tin and tellurium.[1] We shall compare these dependences in a manner similar to that used by us earlier, and we shall not repeat the details.

The dependence of ICS for the six-coordination compounds of antimony on the difference of the electronegativity ΔX turns out to be linear, just as in the case of the six-coordination compound of tin and tellurium. Inasmuch as tin and antimony form identical chemical bonds in the compounds under consideration, via sp^3d_2 hybridization (from this point of view, these compounds can be called isoelectronic), the electron density at the Sn^{119} and Sb^{121} nuclei should change in the same direction with increasing ΔX. However, as can be seen from Fig. 3, the sign of the dependence of the ICS on the value of ΔX for compounds of antimony and tin turns out to be different. Hence, taking into consideration the expression for the isomer shift

$$\delta E = K(Z)\frac{\delta R}{R}\,\Delta\psi^2(0), \quad (2)$$

we can directly conclude that the sign of the change of the charge radius of the nucleus, δR/R, should be different for Sn^{119} and Sb^{121}. By now it has been established[11–13] that δR/R > 0 for the 23.8-keV γ transition in Sn^{119}. Consequently, δR/R is negative for the 37.2-keV γ transition.

The relative quantity

$$\nu \equiv \frac{(\delta R/R)_{\mathrm{Sb}}}{(\delta R/R)_{\mathrm{Sn}}}$$

can be determined from the following expression

$$\nu = \frac{\delta E(\mathrm{Sb})_{\Delta X=1}}{\delta E(\mathrm{Sn})_{\Delta X=1}}\,\frac{K(Z)_{\mathrm{Sn}}}{K(Z)_{\mathrm{Sb}}}\,\frac{\Delta\psi^2(\mathrm{Sn})_{\Delta X=1}}{\Delta\psi^2(\mathrm{Sb})_{\Delta X=1}}. \quad (3)$$

The values of δE corresponding to unity difference of the electronegativity turned out to be as follows: $\delta E(\mathrm{Sb})_{\Delta X=1} = 62.5 \times 10^{-8}$ eV and $\delta E(\mathrm{Sn})_{\Delta X=1} = 8.8 \times 10^{-8}$ eV. The ratio of the nuclear factors $K(Z)_{\mathrm{Sn}}/K(Z)_{\mathrm{Sb}}$ was calculated with allowance for relativistic corrections[14] and found to be

$$\frac{K(Z)_{\mathrm{Sn}}}{K(Z)_{\mathrm{Sb}}} = \frac{1{,}44\cdot 10^{-29}\,\mathrm{eV\text{-}cm^3}}{1{,}55\cdot 10^{-29}\,\mathrm{eV\text{-}cm^3}} = 0{,}93.$$

Further, with the aid of the nonrelativistic single-electron wave functions[15] we obtain

$$\frac{\Delta\psi^2(\mathrm{Sn})_{\Delta X=1}}{\Delta\psi^2(\mathrm{Sb})_{\Delta X=1}} = \frac{\psi_{5s}{}^2(\mathrm{Sn})}{\psi_{5s}{}^2(\mathrm{Sb})} = \frac{1.12\cdot 10^{26}\,\mathrm{cm}^{-3}}{1.34\cdot 10^{26}\,\mathrm{cm}^{-3}} = 0.84.$$

Using these results we get from (3) the connection between the relative changes of the mean-square charge radii for two Mössbauer γ transitions (23.8 keV in Sn^{119} and 37.2 keV in Sb^{121}) a value ν = −(5.5 ± 0.3). This value agrees well with the preliminary estimate ν ≅ −6, which we obtained earlier[1] in comparison of the values of the ICS for the pairs $Sn^{121}O_2$—Sb^{121} and $Sn^{119}O_2$—β-Sn^{119} under the assumption that the chemical bond of the antimony atoms in the SnO_2 lattice differs little from the bonds of tin in the same lattice.

If it is assumed that $(\delta R/R)_{\mathrm{Sn}} = 3.3 \times 10^{-4}$,[13] then we get

$$(\delta R/R)_{\mathrm{Sb}} = -18.1\cdot 10^{-4}. \quad (4)$$

However, the value of $(\delta R/R)_{\mathrm{Sn}}$ was obtained in [13] with accuracy of approximately 30%. We emphasize that in principle a more accurate is a ratio ν that depends little on the degree of approximation used in the calculation of the electron wave functions $\psi^2(0)$ and the absolute values of the ionicity of the bonds.

We can attempt to estimate $(\delta R/R)_{\mathrm{Sb}}$ by an independent method, by determining the shift δE corresponding to total detachment of valence 5s-electron. Figure 3 shows the value of the ICS for the compound InSb, in which a practically fully covalent sp^3-hybrid bond is realized[16] (to a certain degree, the compound InSb can be regarded as the analog of gray tin β-Sn when dealing with problems connected with the calibration of the values of the ICS). If it is assumed that a 50% ionic bond takes place at ΔX = 2,[17] then we can obtain from Fig. 3 that detachment of one 5s-electron in octahedral antimony compounds corresponds to a

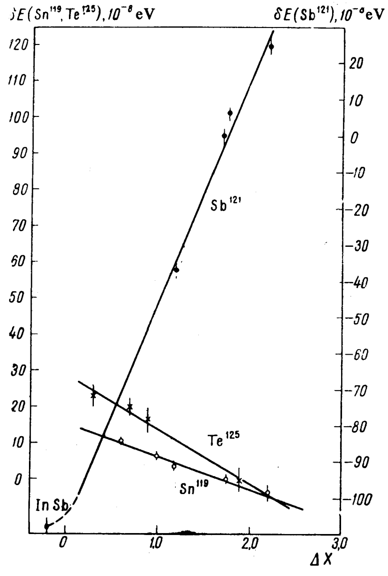

FIG. 3. Dependence of the ICS (δE) of the 37.2-keV γ transition in the Sb^{121} nucleus on the difference ΔX of the antimony-ligand electronegativity for six-coordination components of antimony.

shift $\delta E = 250 \times 10^{-8}$ eV. Allowance for the screening action of the d-electrons (amounting to about 15%, as shown in [1]) yields for the shifts due to one 5s-electron in the antimony atom a value $\delta E = 290 \times 10^{-8}$ eV. Using the foregoing values of $K(Z)_{Sb}$ and $\psi_{5s}^2(0)$, we obtain with the aid of (2)

$$(\delta R / R)_{Sb} = -14.4 \cdot 10^{-4}.$$

This quantity (with allowance for the experimental error in [13]) does not contradict the result (4) obtained above.

Considerations connected with the screening role of the d-electron follow also from a comparison of the values of the ICS for the complex salt $HSbCl_6 \cdot xH_2O$ and $SbCl_5$. Antimony pentachloride has a trigonal bipyramidal structure, wherein the antimony atom forms five sp^3d-hybrid bonds with the chlorine.[18] As seen from the table, the absolute value of the ICS between $SbCl_5$ and $HSbCl_6 \cdot xH_2O$ is 0.5 mm/sec, corresponding to a larger density of the s-electron $\psi_s^2(0)$ in the $SbCl_5$. This result can be attributed to the fact that in the case of the sp^3d-hybrid bond the d-electrons exert a smaller screening action compared with the screening in the sp^3d^2 bond.

In conclusion we note that during the time that we measured the Mössbauer effect on Sb^{121} there was published a brief communication[19] in which ν was assigned a value 3–4. Since this communication was by way of a summary, we cannot discuss this result.

---

[1] V. S. Shpinel', V. A. Bryukhanov, V. Kotkhekar, and B. Z. Iofa, Zh. Eksp. Teor. Fiz. **53**, 23 (1967) [Sov. Phys.-JETP **26**, 16 (1968)].

[2] R. E. Snyder and G. B. Beard, Phys. Lett. **15**, 264 (1965).

[3] Yu. Kagan, Zh. Eksp. Teor. Fiz. **41**, 659 (1961) [Sov. Phys.-JETP **14**, 472 (1962)].

[4] E. H. Hygh and T. P. Das, Phys. Rev. **143**, 452 (1966).

[5] R. L. Mössbauer and W. H. Wiedemann, Z. Physik **159**, 33 (1960).

[6] Pham. Zui hien and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **44**, 393 (1963) [Sov. Phys.-JETP **17**, 288 (1963)].

[7] B. F. Ormont, Struktury neorganicheskikh veshchestv (Structures of Inorganic Substances), Gostekhizdat, 1950.

[8] N. Schreweling, Z. Anorg. Allgem. Chem. **238**, 245 (1938).

[9] L. Pauling, The Nature of Chemical Bonds, Ithaca, N. Y., 1960.

[10] M. Finemann, J. Chem. Phys. **62**, 947 (1958).

[11] V. A. Bryukhanov, N. N. Delyagin, A. A. Opalenko, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **43**, 432 (1962) [Sov. Phys.-JETP **16**, 310 (1963)].

[12] J. Lee and P. A. Flinn, Phys. Lett. **19**, 186 (1965).

[13] J. P. Bocgnet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, Phys. Rev. Lett. **17**, 809 (1966).

[14] D. A. Shirley, Revs. Modern Phys. **36**, 339 (1964).

[15] F. Hermann and S. Skillmann, Atomic Structure Calculations, Prentice Hall, 1963.

[16] R. W. G. Wyckoff, Crystal Structure, Interscience, 1948.

[17] L. Pauling, J. Chem. Phys. **56**, 361 (1952).

[18] S. M. Ohlberg, J. Am. Chem. Soc. **81**, 811 (1959).

[19] G. M. Kalvions, S. L. Ruby, R. E. Snyder, and G. B. Beard, Bull. Am. Phys. Soc. **11**, 369 (1966).

Translated by J. G. Adashko
184