SOVIET PHYSICS JETP VOLUME 26, NUMBER 1 JANUARY, 1968

ISOMER CHEMICAL SHIFTS OF THE MOSSBAUER γ LINE IN ISOELECTRONIC TIN AND TELLURIUM COMPOUNDS

V. S. SHPINEL, V. A. BRYUKHANOV, V. KOTKHEKAR, and B. Z. IOFA

Nuclear Physics Institute, Moscow State University

Submitted January 2, 1967

Zh. Eksp. Teor. Fiz. **53**, 23—28 (July, 1967)

Isomer chemical shifts (ICS) of the Mossbauer γ line in isoelectron tin complexes of the $SnHal_6^{-2}$ type and tellurium complexes of the $TeHal_6^{-2}$ type (Hal = F, Cl, Br, I) are studied. A comparison of the dependence of the magnitude of the ICS on the electronegativity of the halide for both types of complexes shows that the sign of change of the nuclear charge $\rho = \delta R/R$ for the 35.6-keV γ transition in the Te^{125} nucleus is the same as that for the 23.8-keV γ transition in the Sn^{119} nucleus, that is, it is positive. The value of $\rho(Te)/\rho(Sn)$ has also been obtained and found to equal 1.1. Calibration of the ICS for the 25.6-keV γ transition in the Te^{125} nucleus corresponding to a single 5s-electron is carried out. Finally, preliminary measurements of the magnitude of the ICS for the Sb^{121} 37.5-keV γ line are made, which yield $\rho(Sb)/\rho(Sn) \approx -6$.

As shown in [1], the isomer chemical shifts (ICS) of the Mossbauer γ line reveal, for the isoelectronic tin compounds of the $SnHal_4$ type, a clear-cut correlation with the electronegativity of the halide atoms. Such a correlation makes it possible to relate more reliably the values of the ICS with the character of the chemical bond in the investigated compounds, and is important in the analysis of the experimental data obtained with the aid of the nuclear γ-resonance method. In order to determine from the ICS data the change in the charge radius of the nucleus $\rho = \delta R/R$, occurring during the resonant transition, it becomes necessary to calculate the electron density in the nucleus of a many-electron atom in a molecule or in a crystal. These calculations cannot be performed at present with high accuracy, and the values of ρ obtained thereby are not reliable enough.

Additional useful information, which does not call for absolute calculations of the electron density at the Mossbauer nucleus, can be obtained in the investigation of ICS in isoelectronic compounds of elements having the valence electrons in one and the same shell, for example tin and tellurium, which have outer-electron configurations $5s^2 5p^2$ and $5s^2 5p^4$, respectively. One of the most essential results of this kind of investigation may be the determination of the relative values of ρ for both nuclei.

The present paper is devoted to a comparison of the values of the ICS of the Mossbauer γ line in isoelectronic complexes of tellurium, of the type $TeHal_6^{-2}$, and complexes of tin of the type $SnHal_6^{-2}$ (Hal = F, Cl, Br, I). The choice of these complexes for the investigation is connected with the fact that, in spite of the difference in the configuration of the valence shell, the character of the chemical bond of tin and tellurium is the same in these complexes. Indeed, both $TeHal_6^{-2}$ and $SnHal_6^{-2}$ are octahedra of the symmetry group O_h^5 [2], in which the tellurium and the tin form equivalent bonds with six halides. It is customary to assume (for example, [3]), that in this case the chemical bond of the central atom (tellurium or tin) with the ligands is based on sp^3d^2 hybridization.

The values of the ICS of the 35.6-keV γ transition of Te^{125} in complexes of the type $TeHal_6^{-2}$ were measured by us earlier.[4] In connection with the fact that until recently there were no systematic data on the ICS in complexes of the $SnHal_6^{-2}$ type, we have also measured the ICS of the 23.8-keV γ transition of Sn^{119} for a number of six-coordination compounds of tin of the type Me_2SnHal_6, and also for the compounds $Me_2Sn(OH)_6$ (in the different compounds, Me corresponds to the following cations: H^+, Na^+, $(NH_4)^+$, K^+, Rb^+, Cs^+).

Measurements of the resonance-absorption spectra for the indicated compounds were made with an electrodynamic Mossbauer setup operating in the constant-velocity mode.

To register the resonance γ radiation we used a standard scintillation spectrometer with FÉU-13B photomultiplier and NaI(Tl) crystal (1 mm thick). The source of the 23.8-keV resonance quanta was

Values of ICS for complex compounds of tin and tellurium

Compound	ICS (δE)		Compound	ICS (δE)	
	mm/sec	eV × 10^{-8}		mm/sec	eV × 10^{-8}
Na_2SnF_6	—0.48±0,05	—3.8±0.4	$Na_2Sn(OH)_6$	0.02±0,05	0.16±0.4
H_2SnCl_6	0.50±0,05	4.0±0.4	$K_2Sn(OH)_6$	0.03±0,05	0.24±0.4
$(NH_4)_2SnCl_6$	0.48±0,05	3.8±0.4	TeF_6^{-2}	0.0 ±0,3	0.0 ±3.5
K_2SnCl_6	0.45±0,05	3.6±0.4	$TeCl_6^{-2}$	1.4 ±0,3	16.6 ±3.5
Rb_2SnCl_6	0.43±0,05	3.4±0.4	$TeBr_6^{-2}$	1.7 ±0,3	20.1 ±3.5
Cs_2SnCl_6	0.45±0,05	3.6±0.4	TeI_6^{-2}	2.0 ±0,3	23.7 ±3.5
$(NH_4)_2SnBr_6$	0.80±0,05	6.4±0.4			
K_2SnBr_6	0.75±0,05	6.0±0.4			
Rb_2SnI_6	1.35±0,05	10.6±0.4			

$BaSnO_3$. The measurements were made at liquid-nitrogen temperature.

The table lists the obtained values of the ICS for the compounds indicated above (the shifts given for the tellurium compounds were taken from [4]). In the case of the tin complexes, the shifts are given relative to SnO_2. For the tellurium complexes the ICS are given relative to Te^{125}(Cu).

For all the complexes of the $SnHal_6^{-2}$ type, the resonance absorption spectrum was singlet line of a width indicating the absence of a noticeable quadrupole interaction. This result is natural, since, as indicated above, tin forms in the $SnHal_6^{-2}$ complex six symmetrical equivalent bonds with six halides. The absorption line in the samples $K_2Sn(OH)_6$ and $Na_2Sn(OH)_6$ turned out to be broadened (broadening on the order of 50%), this being apparently connected with the noncubic structure of these compounds[5].

An investigation of the complexes $SnHal_6^{-2}$ with different cations in the external coordination sphere was carried out by us in connection with the fact that there are published data[6] indicating that the tin-ligand bond lengths depend on the character of the cation. As seen from the table, the values of the ICS depend only on the ligand and do not depend, within the limits of experimental error, on the character of the cation.

The dependence of the values of the ICS (δE) on the difference (ΔX) between the electronegativities of the tin-ligand and the tellurium-ligand (the values of ΔX are taken from the papers of Pauling[7] and Finemann[8]), shown in the figure, can be regarded as linear in the central section, just as in the case of compounds of the type $SnHal_4$[1]. Actually, the dependence of δE on the degree of ionicity of the bond should be linear. Since the connection between the ionicity and ΔX is nonlinear near the purely covalent and purely ionic bonds[7], the observed dependence should also deviate from linear at the beginning and at the end of the curve. Comparison of these relationships makes it possible to draw the following conclusions:

1. The expression for the ICS, as is well known, has the following form:

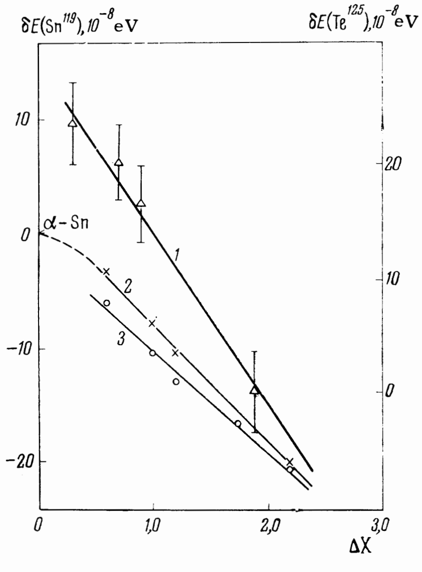
$$\delta E = K(Z)\rho\Delta\Psi^2(0), \qquad (1)$$

where K(Z) is the atomic factor, $\rho = \delta R/R$ is the relative change in the charge radius of the nucleus during the resonant transition, $\Delta\Psi^2(0)$ is the difference between the electronic densities at the Mossbauer nucleus in the source and in the absorber. As seen from the diagram, the sign of the dependence of δE on the values of ΔX is the same for the tin and tellurium complexes under consideration. Inasmuch as tin and tellurium form the same chemical bonds in these compounds, it is natural to assume that the electron density at the nuclei Sn^{119} and Te^{125} likewise changes in one direction when ΔX is changed. It therefore follows from (1) that the sign of the change in the charge radius of the nucleus should be the same for the transitions under consideration in the Sn^{119} and Te^{125} nuclei.

It has by now been established[9-11] that $\rho > 0$ for the 23.8-keV γ transition in Sn^{119}. Consequently, ρ is likewise positive for the 35.6-keV γ transition in Te^{125}.

The decrease in the values of the ICS with increasing electronegativity of the ligand shows also that the principal factor determining the values of $\Psi^2(0)$ in the investigated complexes of tellurium and tin is the degree of "drawing" of the s-electrons to the ligand. This conclusion agrees with the results of theoretical calculations based on relativistic electron functions[10,11], from which it follows that for tin compounds the change of $\Psi^2(0)$ due to screening of the internal s-electrons is of the order of 20% of the $\Psi^2(0)$ corresponding to one 5s-electron.

2. The plots of the ICS presented in the figure for the complexes $TeHal_6^{-2}$ and $SnHal_6^{-2}$ make it possible to obtain the values of δE corresponding



ICS for the 23.8-keV γ transition in Sn^{119} and the 35.6-keV transition in Te^{125} vs. the difference of the tin-ligand and tellurium-ligand electronegativities: 1 – Complexes of the $TeHal_6^{-2}$ type (δE relative to Te^{125} (Cu)); 2 and 3 – tetrahalides of tin (from data of [1] and, respectively, six-coordination complexes of tin (δE relative to α-Sn).

to a unit difference of electronegativity. We obtained the following values:

$$\delta E(\mathrm{Te})_{\Delta X=1} = 15\cdot 10^{-8}\,\mathrm{eV}, \quad \delta E(\mathrm{Sn})_{\Delta X=1} = 8.8\cdot 10^{-8}\,\mathrm{eV}.$$

From this we can determine $\rho(\mathrm{Te})/\rho(\mathrm{Sn})$, since we have, taking (1) into account,

$$\frac{\rho(\mathrm{Te})}{\rho(\mathrm{Sn})} = \frac{\delta E(\mathrm{Te})_{\Delta X=1}}{\delta E(\mathrm{Sn})_{\Delta X=1}}\,\frac{K(Z)_{\mathrm{Sn}}}{K(Z)_{\mathrm{Te}}}\,\frac{\Delta\Psi^2(\mathrm{Sn})_{\Delta X=1}}{\Delta\Psi^2(\mathrm{Te})_{\Delta X=1}}. \quad (2)$$

The atomic factors with allowance for relativistic corrections were calculated with the aid of the expressions given by Shirley[12] and found to be

$$K(Z)_{\mathrm{Sn}} = 1.44\cdot 10^{-29}\,\mathrm{eV\text{-}cm^3}, K(Z)_{\mathrm{Te}} = 1.63\cdot 10^{-29}\,\mathrm{eV\text{-}cm^3}.$$

To calculate the ratio $\Delta\Psi^2(\mathrm{Sn})_{\Delta X=1}/\Delta\Psi^2(\mathrm{Te})_{\Delta X=1}$ we used the nonrelativistic single-electron wave functions[13], taking into account the obvious relation

$$\Delta\Psi^2(\mathrm{Sn})_{\Delta X=1} / \Delta\Psi^2(\mathrm{Te})_{\Delta X=1} = \Psi_{5s}{}^2(\mathrm{Sn}) / \Psi_{5s}{}^2(\mathrm{Te}).$$

The calculation performed in this manner gave the following values:

$$\Psi_{5s}{}^2(\mathrm{Sn}) = 1.1\cdot 10^{26}\,\mathrm{cm^{-3}}, \qquad \Psi_{5s}{}^2(\mathrm{Te}) = 1.5\cdot 10^{26}\,\mathrm{cm^{-3}}.$$

From this we get

$$\Delta\Psi^2(\mathrm{Sn})_{\Delta X=1}/\Delta\Psi^2(\mathrm{Te})_{\Delta X=1} = 0.7.$$

Using these results we obtain with the aid of (2) a connection between the relative changes of the mean-square charge radii of the nucleus for the two Mossbauer γ transitions, 23.8 keV in Sn^{119} and 35.6 keV in Te^{125}:

$$\rho(\mathrm{Te})/\rho(\mathrm{Sn}) = 1.1.$$

It must be emphasized that this result does not depend on the degree of approximation of the calculation of the electron wave functions (only their ratio is important), or on the absolute values of the degree of ionicity of the bonds, and is in principle more reliable than an estimate of the absolute values of ρ from the calculated values of $\Psi^2(0)$.

If we assume that $\rho(\mathrm{Sn}) = 3.3 \times 10^{-4}$ (the result obtained by Bocquet et al.[11] by measuring the spectra of the internal-conversion electrons for the 23.8-keV transition in β-Sn and in SnO_2), then we get $\rho(\mathrm{Te}) = 3.6 \times 10^{-4}$ for the 35.6-keV γ transition in Te^{125}.

3. Comparison of the variation of the values of the ICS for complex compounds of tin and tetrahalides of tin, $SnHal_4$, shows that the density of the s-electrons at the Sn^{119} nuclei in octahedral compounds ($5sp^3d^2$ hybridization) is smaller by almost 15% than in the case of tetrahedral compounds, in which the bond between the tin and halides is formed by $5sp^3$ hybridization. This result can be attributed to the screening action of the d-electrons in the hybrid $5sp^3d^2$ bond.

4. The dependence of the ICS in $TeHal_6^{-2}$ complexes on the electronegativity of the ligand can be used for an independent estimate of $\rho(\mathrm{Te})$, if we extrapolate the values of δE to the fully covalent and fully ionic bond, i.e., if we determine the value of δE corresponding to detachment of one 5s-electron. To this end it is possible to use data on the relation between the degree of ionicity of the bonds and the values of ΔX given by Pauling[14]. It is seen from these data that when $\Delta X = 2$ there is realized approximately 50% ionic bond. From this we get that detachment of one 5s-electron in the octahedral compounds of tellurium corresponds to a shift equal to 60×10^{-8} eV. Allowance for the screening action of the d-electrons (a quantity on the order of 15%, as noted above), gives a value of 70×10^{-8} eV for the shift due to one 5s-electron in the tellurium atom. Using the values of $K(Z)_{\mathrm{Te}}$ and $\Psi_{5s}^2(\mathrm{Te})$ obtained above, we get from (1) $\rho(\mathrm{Te}) = 2.8 \times 10^{-4}$. This agrees with the value $\rho(\mathrm{Te})$ obtained from the ratio $\rho(\mathrm{Te})/\rho(\mathrm{Sn})$, since the value of $\rho(\mathrm{Sn})$ in [11] is determined with an accuracy of approximately 30%.

5. Among the tellurium compounds investigated to date, a reliable estimate of the number of valence electrons in the 5s-state has been made only for metallic tellurium[15]. This value turns out to be 1.6. The value of the ICS obtained by extrapolat-

ing the observed $\delta(E)$ plot to the fully covalent bond ($\Delta X = 0$), corresponding to one 5s-electron in octahedral tellurium complexes, is much larger than the value of δE for metallic tellurium, the latter being 7.5×10^{-8} eV relative to $Te^{125}(Cu)$. It can be assumed that this circumstance is due to the additional density produced by the non-bonding pair of 6s-electrons. The hypothesis that such electron pairs can exist in complexes of the $TeHal_6^{-2}$ type was advanced by Pauling[7]. Apparently, donor electrons of the external cations participate in the formation of such a pair. Using the calibration obtained above for the values of the ICS, we can show that the additional density of this non-bonding pair of 6s-electrons $\Psi^2(0)$ at the Te^{125} nuclei is of the order of half the density corresponding to one 5s-electron. We have made an approximate estimate of $\Psi^2(0)$ for a pair of 6s-electrons, using the spectroscopic data for the tellurium atom[16] and the Fermi-Segre formula[17]. The calculated value turned out to be approximately half the value obtained by the method indicated above.

We are presently continuing the investigations of the values of the ICS of the resonant γ line in isoelectronic compounds also for the case of the 37.2-keV γ transition in Sb^{121}, which in turn will yield information on the value of $\rho(Sb)$. Preliminary results obtained by us in observation of the Mossbauer effect on Sb^{121} make it possible to estimate the ratio $\rho(Sb)/\rho(Sn)$. The value of the ICS of the 37.2-keV γ transition, for a source in the form $Sn^{121}O_2$ turned out to be approximately -12 mm/sec relative to metallic antimony (the shift of the resonant line for a source in the form of metallic β-Sn^{121} relative to antimony is close to zero[18]). If we assume that the character of the chemical bond of the antimony atoms in the SnO_2 lattice differs little from the bonds of the tin atoms in the same lattice, then a comparison of the shifts of the resonance line for the pairs $Sn^{121}O_2$-Sb and $Sn^{119}O_2$-β-Sn yields for the ratio a value $\rho(Sb)/\rho(Sn) \approx -6$.

The authors are grateful to E. Grishin and V. Makhaev for help in the work.

---

[1] A. Yu. Aleksandrov, N. N. Delyagin, K. P. Mitrofanov, L. S. Polak, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **43**, 1242 (1962) [Sov. Phys.-JETP **16**, 879 (1963)].

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

[3] Poluprovodnikovye veshchestva. Voprosy khimicheskoi svyazi (Semiconductor Substances, Problems of the Chemical Bond), Collection of translations edited by V. P. Zhuze, IIL, 1960.

[4] V. A. Bryukhanov, B. Z. Iofa, A. A. Opalenko, and V. S. Shpinel', ZhNKh (J. of Inorganic Chemistry) **12**, No. 7 (1967).

[5] J. D. Dannag, N. Nowacki, and J. Dannag, Crystal data classification of substances by space groups and their identification from cell dimension, New York, (1954).

[6] G. Engel, Z. Kristal. **90**, 341 (1935).

[7] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, 1960.

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

[9] 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)].

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

[11] J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, Preprint, CALT-63-39.

[12] D. A. Shirlety, Revs. Modern Phys. **36**, 339 (1964).

[13] F. Hermann and S. Skillman, Atomic Structure Calculations, Prentice Hall, 1963.

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

[15] C. E. Violet and R. Booth, Phys. Rev. **144**, 225 (1966); C. E. Violet, R. Booth, and E. Wooten, Phys. Lett. **5**, 230 (1963).

[16] Atomic Energy Levels as Derived From Optical Spectra. Ed. C. E. Moore, Circular of the National Bureau of Standards, N467 (1949).

[17] E. Fermi and E. Segre, Z. Physik **82**, 729 (1933).

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

Translated by J. G. Adashko
3