CHEMICAL EFFECT ON OUTER-SHELL INTERNAL CONVERSION IN Sn^{119}; INTERPRETATION OF THE MÖSSBAUER ISOMER SHIFT IN TIN*

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With Sn^{119m} sources in two different chemical forms, high-resolution internal-conversion measurements were made of electron lines from the 23.87-keV $M1$ transition. It was found that the $5s$ (valence-shell) electron density near the nucleus is about 30% smaller in SnO_2 than in white tin; calculations show that roughly 17% of this decrease in $5s$ electron density is compensated for by an increase in the sum of $1s$, $2s$, $3s$, and $4s$ densities. With this information on s electron densities and from the value of the Mössbauer chemical isomer shift between white tin and SnO_2, it has been possible to conclude that the nuclear charge radius of the 23.87-keV state of Sn^{119} is 3.3×10^{-4} larger than that of the ground state.

In a number of experiments[1] the state of chemical binding has been shown to affect the rate of radioactive decay; however, the interpretation of these results has been uncertain because of lack of knowledge of the effects of binding on electron wave functions for the several atomic shells. The results reported in this Letter concern the effect of change in chemical state on the relative rates of internal conversion in the various individual shells. The transition studied was the 23.87-keV transition (essentially pure $M1$)[2,3] occurring in the decay of 250-day Sn^{119m}.

The principal comparison was between sources in the form of white tin metal and of stannic oxide, SnO_2. These sources were prepared from neutron-irradiated, highly enriched Sn^{118}, which was used as source material[4] in an electromagnetic isotope separator. The mass-119 ion beam was retarded to 1.5 keV just before it reached the collector in order to produce an effective source thickness of about 2 $\mu g/cm^2$; the chemical form of the sample was determined by choice of appropriate collector foil and by subsequent treatment when required. In order to identify the final chemical form of the samples used for the internal-conversion measurements, the recoil-free resonance spectra of the 23.87-keV gamma rays were examined with a Mössbauer velocity spectrometer.

Figure 1 shows the Mössbauer absorption spectra for some of these sources taken with a white-tin absorber. Absorption spectra taken with an ordinary white-tin source and absorbers of white tin, SnO, and SnO_2 are also shown for comparison. Although the spectra obtained from the sources prepared in the separator show somewhat broadened peaks with evidence of some impurity, their major constituents are clearly identified as white tin and SnO_2, respectively.

Measurements of the internal conversion-electron spectra were made with a 50-cm, double-focusing, iron, beta-ray spectrometer at momentum resolutions of 0.10 to 0.15% A proportional counter having a window about 50 $\mu g/cm^2$ thick was used as detector; window absorption corrections were thus negligible. All the conversion lines of the 23.875-keV transition as well as those of the preceding 65.66-keV $M4$ transition were measured.[5] It was found that the relative intensity of the 23.875-keV O line was dependent on the chemical form of the source, whereas relative intensities of all the other conversion lines were constant, within the experimental accuracy of about 3 or 4%. It was not possible to obtain useful information about the 65.66-keV O line, because of inadequate resolution in this energy region. In Fig. 2 there are shown for comparison the conversion-electron spectra, in the region of the 23.875-keV N and O lines, from sources of white tin and SnO_2. Analysis of the spectra for determination of the 23.875-keV N and O line intensities was made with the aid of information about the relative energies and intensities of the K-LM Auger lines present on both sides of the O line. This information was based on published data[6] concerning the K-LM spectrum of Ag and on measurements of the K-$L_2M_{2,3}$ and K-$L_3M_{2,3}$

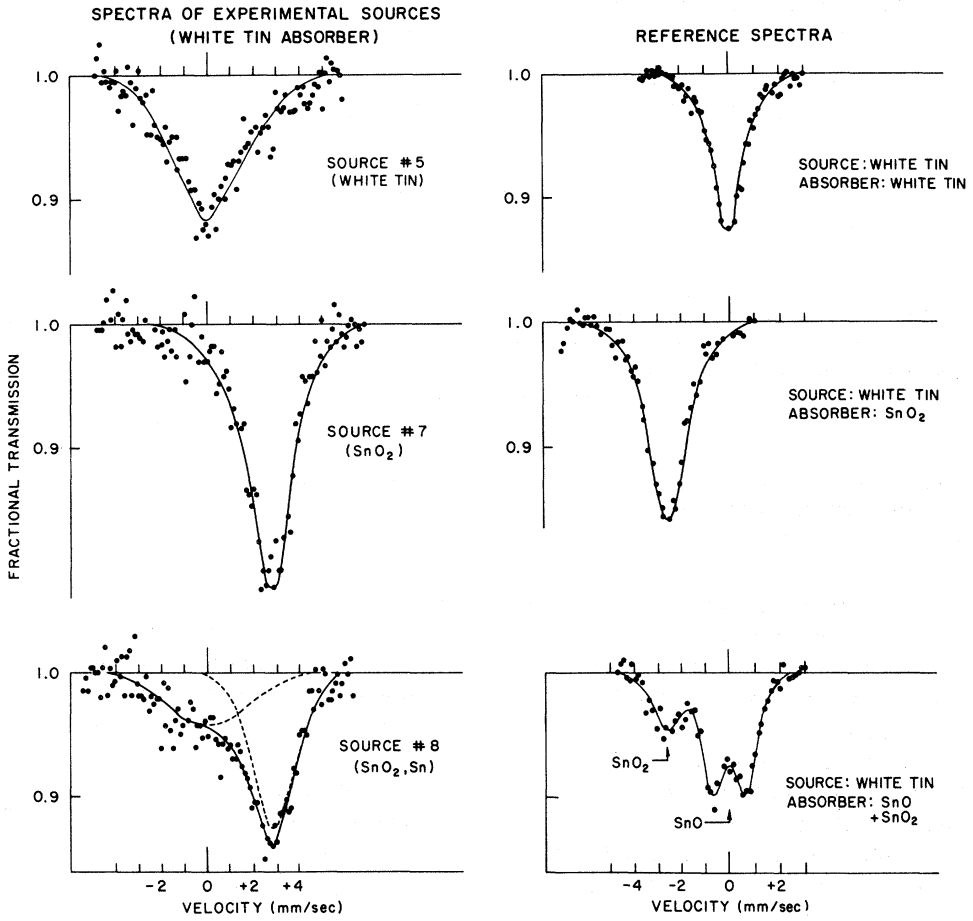

FIG. 1. Mössbauer spectra of the Sn^{119m} internal-conversion sources measured with a white-tin absorber. Chemical forms of these sources were white tin, SnO_2, and a mixture of SnO_2 and an impurity whose isomer shift corresponds to that of white tin or SnO. For comparison there are shown three "standard" spectra taken with an ordinary white-tin source and absorbers of white tin, of SnO_2, and of SnO. Note that the isomer shifts of the "standard" spectra are opposite in sign to those of the internal-conversion sources.

lines observed in the spectrum just above the N-O-Auger complex from the Sn^{119m} sources. Results of the analyses of seven spectra obtained with four sources are given in Table I. With each N/O ratio is given the N/K-$L_1M_{2,3}$ ratio. The intensity of the very weak K-$L_1M_{2,3}$ line, which was actually determined in the unfolding of the N-O-Auger complex, was found to be constant, within about 10%, relative to the N-line intensity. This shows that errors in the background corrections and uncertainties in the spectrum analysis are small compared with the difference in N/O ratio between the two types of sources. The uncertainty given with each ratio represents an estimate of the standard deviation made with consideration given to statistics of the counting and to uncertainty in the analysis. For source No. 8 the Mössbauer spectrum indicated that only about 60% of the material was in the form of SnO_2, the rest having an isomer shift similar to that of white tin or SnO. The N/O ratio, 11.5, observed for this source may be corrected on the assumption that the ~40% was indeed of the composition of source No. 4 or No. 5; and the resulting value 13.3 is given in brackets. With this value, the SnO_2 average becomes 13.6 ± 0.6. The white tin average is 9.3 ± 0.3. Both of these ratios may be a few percent too low because of a small contribution to the "O" line by conversion electrons from the $N_{4,5}$ levels. The conclusion is that the conversion in the O shell is about 30% smaller in SnO_2 than it is in white tin.

Internal conversion of magnetic dipole tran-

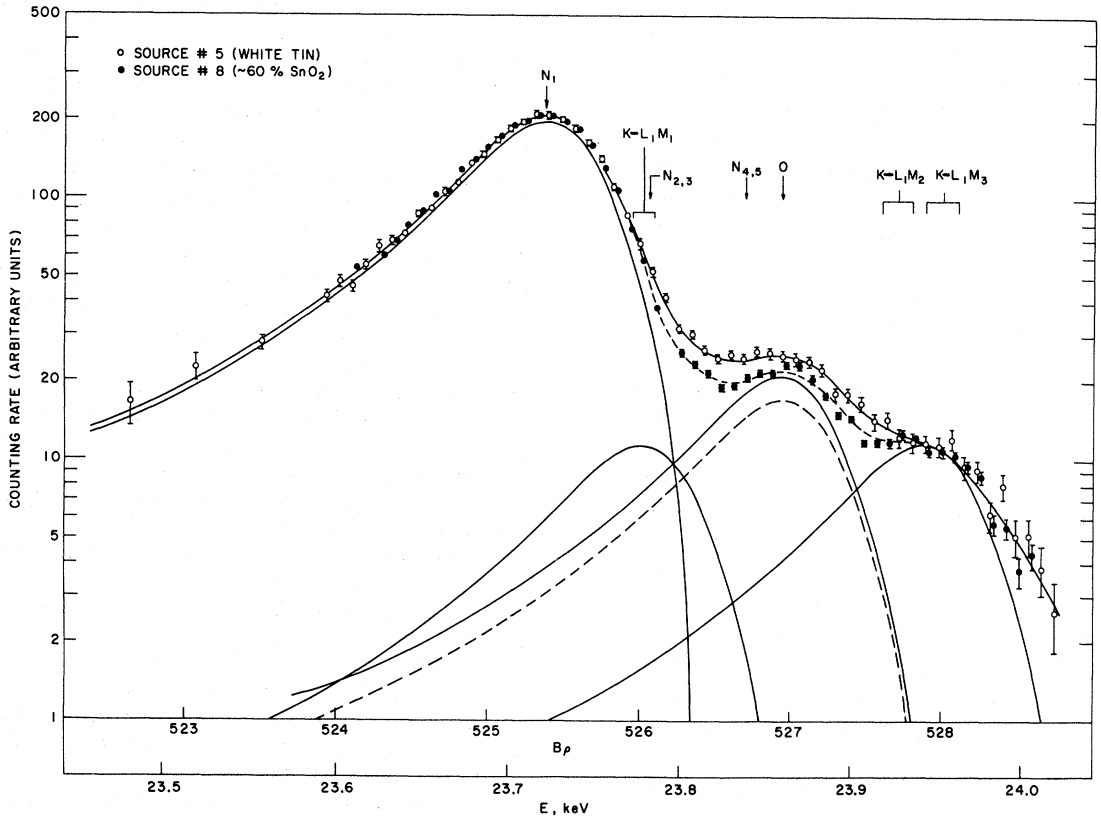

FIG. 2. Electron spectra from two different Sn^{119m} sources, one in the form of white tin and one mainly of SnO_2. The *N* and *O* conversion lines of the 23.87-keV transition and two *K-LM* Auger lines are shown. The curves have been normalized to equal *N* line intensity. The white-tin source, which was narrower than the other, was slightly misoriented for this measurement to produce a line shape very nearly matching that of the SnO_2 source. The resolution into the several components shown is approximate and is intended for illustration; it is not exactly the same as the best resolutions of the separate spectra which were actually used as final results.

Table I. Relative intensities of *N* and *O* lines from internal conversion of the 23.875-keV, *M*1 transition in Sn^{119m}. Sources were in two chemical forms, white tin and SnO_2. The value in brackets for source No. 8 includes a correction described in the text which was made to take into account the fact that this source was only 60% SnO_2. See text for significance of third column.

Source	*N/O*	$N/K\text{-}L_1M_{2,3}$
No. 7 SnO_2	15.0 ± 2.7	18.8
	13.6 ± 0.9	18.0
No. 8 60% SnO_2	11.5 ± 0.5 → [13.3 ± 0.9]	17
No. 4 white tin	9.1 ± 1.3	15
	10.0 ± 0.8	16
No. 5 white tin	9.1 ± 0.4	15
	9.4 ± 0.4[a]	17
	Weighted averages	
SnO_2	12.1 ± 0.4 → [13.6 ± 0.6]	18
white tin	9.3 ± 0.3	16

[a]Source tilted to worsen resolution.

sitions is dominated by terms whose matrix elements at low and moderate energies are proportional to the magnitude of the bound-state electron wave functions near the nucleus[7]; thus most of the process occurs for *K*, L_1, M_1, and N_1 initial states with *s* outgoing waves. One then expects that the rate of *O*-shell conversion is proportional to the density of 5*s* electrons near the nucleus. The experimental result therefore shows that this density is about 30% smaller in SnO_2 than in white tin.

Experiments of this type give more direct information about the effects of chemical binding on individual electron wave functions than do experiments on changes of transition half-lives,[1] in which the measured quantity is a complicated function of effects in several electron shells. It may be that results described in this Letter are closely related to the electron binding-energy shifts observed by the Uppsala group.[8]

By combining the information obtained in these measurements on the changes of 5s electron density near the nucleus with data on the Mössbauer isomer shift of SnO_2 relative to white tin, one can obtain the sign and an estimate of the magnitude of the change in nuclear charge radius between the ground and 23.87-keV states of Sn^{119}. In addition to the change in s-electron density measured for 5s, a correction must be included for small changes in inner s-electron density which are associated with the 5s changes. This correction can be estimated in two ways. A perturbation treatment in the manner of Crawford and Schawlow[9] with the Hartree-Fock-Slater wave functions of Herman and Skillman[10] gives the result that the total s-electron density change near the nucleus is 17% less than that which is due to the 5s electrons alone. A second estimate can be derived from some nonrelativistic Hartree-Fock calculations of Watson[11] for Sn^{4+} and Sn^{2+}; the correction factor thus derived is 16%. This N/O information on $|\psi_{5s}(0)|^2$ may be combined with the Hartree-Fock values for $|\psi_{4s}(0)|^2$ to give the quantity $\{|\psi_s(0)_{SnO_2}|^2 - |\psi_s(0)_{Sn}|^2\} = -3.9\times10^{25}$ cm^{-3}. From this value and the observed isomer shift one finds $\Delta R/R = +3.3\times10^{-4}$, where the sign indicates that the charge radius of the excited state is larger than that of the ground state. The uncertainty in this quantity is about 30%. The sign obtained here confirms the original analyses of Kistner, Jaccarino, and Walker, of Boyle, Bunbury, and Edwards, and of Bryukhanov, Delyagin, Opaljenko, and Shpinel[12]; but it disagrees with the conclusions of Bersuker, Goldanskii, and Makarov.[13] The conclusions of this work about $\Delta R/R$ are based more directly on experimental evidence than has heretofore been possible. Nuclear-model calculations of $\Delta R/R$ have given conflicting results.[14]

It is not possible to derive conclusions about the effects of chemical binding on the lifetime of the 250-day, 65.66-keV $M4$ transition directly from the results of these measurements on the 23.87-keV, $M1$ transition; electrons in other than s states contribute to the decay, and the screening of these electrons by the valence electrons may differ from screening effects on s electrons.

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$\Delta R/R \sim +1\times10^{-4}$. V. A. Belyakov, Phys. Letters 16, 279 (1965) gives $\Delta R/R \sim -2.5\times10^{-4}$. Earlier estimates may be found in D. A. Shirley, Rev. Mod. Phys. 36, 339 (1964).

SIGN RATIO AND ABSOLUTE FLUX OF COSMIC-RAY ELECTRONS

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Two balloon flights have been carried out over southern France (vertical geomagnetic cutoff given by Shea, Smart, and McCracken[1] as 5.36 BV) to measure with higher precision the value of the flux of cosmic-ray electrons already reported by the authors at this geomagnetic latitude[2] and to investigate the sign ratio of the electrons of energy about 5 BeV as revealed by the east-west asymmetry of the integral flux. The apparatus used consisted of a multiplate spark chamber containing 5 radiation lengths of lead and triggered for shower detection by a plastic-scintillator counter telescope (see Fig. 1).[2,3] The efficiency of detection of electron showers of 6 BeV was 94%, that of 6-BeV proton interactions 41%, and of noninteracting α particles ~40%. The axis of the chamber was inclined at a constant angle of 38° to the zenith and rotated continuously through azimuth. A flux-gate magnetometer monitored the orientation of the chamber with respect to the geomagnetic field.

Details of the two flights are given in Table I.

The analysis of the data consisted in the scanning of the stereo photos of events which triggered the chamber, of a binary coded series of lamps giving the number of single charged particles passing through the scintillator telescope without interacting in the chamber, and of the telemetered record of the orientation of the chamber.

A total of 238 electron showers in Flight I and 169 electron showers in Flight II were recorded during ceiling. These events were selected by visual criteria, in goemetrical conditions such that the axis of the shower lay within the visual area of the chamber. The geometrical factor corresponding to these conditions is 17 ± 1 cm^2 sr; the dead time imposed after each trigger being 1.02 sec, the relative val-

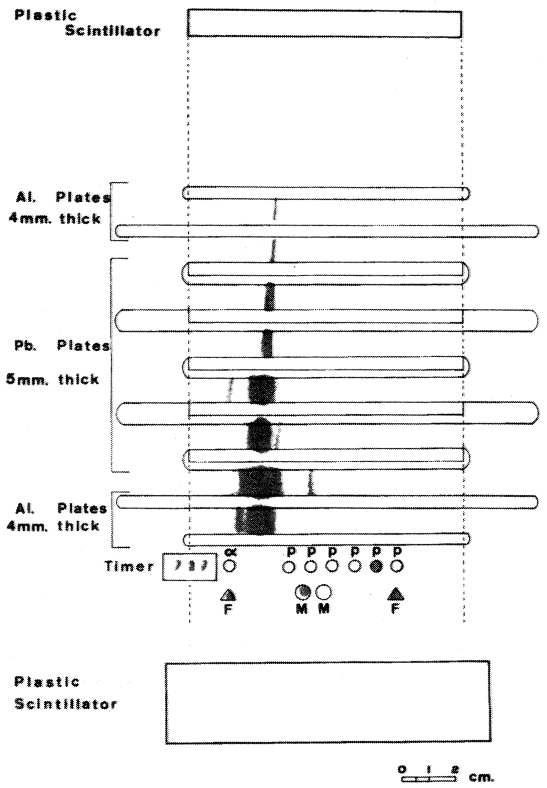

FIG. 1. Photomontage showing an electron shower recorded during the balloon flights and a superimposed sketch of the spark chamber and plastic scintillator telescope. F: fiducial marks for stereoreconstruction of the events; P: binary coded series of lamps giving the number of singly charged particles passing through the scintillator telescope without interacting in the chamber; α: lamp alight when I/I_0 is ≥ 2; M: coded lamps to indicate the geomagnetic quadrant containing the axis of the spark chamber at the moment of trigger.