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# *MÖSSBAUER EFFECT ON* $Sn^{119}$ *NUCLEI AND AN ATTEMPT TO DETECT THE EFFECT IN* $Pr^{141}$

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Isomer shifts of the 23.8-keV $\gamma$ ray from $Sn^{119m}$ were determined in several compounds: $Na_2SnO_3 \cdot 3H_2O$, $SnBr_4$, $SnSO_4$ etc. Quadrupole splitting was found in some of the samples ($SnO_2$, $SnCl_2 \cdot 2H_2O$, etc). The lower limit for the change in the charge radius of $Sn^{119}$ in the excited state was estimated to be $\Delta R/R \geq +0.8 \times 10^{-4}$. Over the range ± 8 mm/sec, to an accuracy of 0.2%, no absorption effect was found for the $7/2^+ \to 5/2^+$ transition with energy 145 keV in $Pr^{141}$.

## INTRODUCTION

A great deal of work has been done on the Mössbauer effect in tin compounds. There are noticeable discrepancies between some of the experimental results. For example, in the experiments of the group at the Nuclear Physics Institute of Moscow State University [1-4] a well-resolved quadrupole splitting was found in polycrystalline $\beta$-tin, whereas in their last experiments [5] and those of other authors [6-8] a much smaller upper limit for this quantity was found. The possible reasons for this disagreement are still not completely explained.

There is interest in studying the Mössbauer spectrum of tin dioxide, which has a tetragonal lattice and is frequently used as a source of radiation.

We have studied the resonance absorption of the 23.8-keV $\gamma$ radiation of $Sn^{119m}$ in various chemical compounds of tin.

The source for the measurements was gray tin, which crystallizes in the diamond lattice and should give an unsplit emission line, as has been confirmed.[10] To our knowledge, other groups have not worked with sources of $\alpha$-tin.

Data were taken on isomer shifts in tin compounds which have not been measured previously. We also describe attempts to detect a Mössbauer effect by absorption and by scattering of the 145-keV $\gamma$ radiation of $Ce^{141}$ in $Pr^{141}$.

## EXPERIMENTAL ARRANGEMENT

For the resonance absorption studies, the source and absorber were placed in styrofoam cryostats and could be cooled to liquid nitrogen temperature. Unless otherwise indicated, the experiments described below were done at this temperature. The absorber cryostat, placed between the detector (a scintillation counter using an FEU-29 photomultiplier with a NaI crystal) and the source cryostat, was set in reciprocating motion using a cam drive. The radiation was recorded only during those parts of the motion when the translational velocity was a given value. During a single cycle of measurements, nine relative velocities (including the null velocity, which was common to all cycles) were given in succession. To do this, after a definite interval we automatically changed the armature voltage of the dc motor, which set in motion a cam gear via a fixed reducing gear. Using velocities determined beforehand in a separate apparatus and employing an interchangeable gear, we could examine the resonance absorption in detail within an arbitrary range of ±8 mm/sec. The instability of the velocity did not exceed ±0.15 mm/sec in the range 1—8 mm/sec and 0.05 mm/sec for velocities up to 1 mm/sec.

The spectrum in the region of the resonance was selected by a single-channel pulse analyzer (AADO-1). The electrical pulses for a definite velocity were recorded in a definite counting channel. To eliminate errors from instability of the equipment which fixed the recording time at different speeds and controlled the switching, separate timing channels were built into the equipment. We thus strictly controlled the time for data collection. The results were recorded relative to the null velocity, thus reducing the effect of slow changes in the parameters of the apparatus.

## EXPERIMENTS WITH TIN COMPOUNDS

Using the apparatus described above, we measured resonance absorption spectra[1] for the 23.8-keV $\gamma$ radiation of $Sn^{119m}$ in 13 different chemical compounds of tin. Two different types of sources were used in the measurements. One was $\alpha$-tin, the other $SnO_2$. The sources were prepared from tin foil, enriched to 94% in $Sn^{118}$ and irradiated in a reactor. The first was gotten by keeping one of the foils for ~15 days at solid oxygen temperature in the presence of a crystallite of gray tin acting as a catalyst. The other was gotten chemically and then annealed for 30 hours at 1200—1400° C to stabilize the crystal structure.

Figure 1 shows the absorption spectra in 9.95 mg/cm$^2$ of $\beta$-Sn and 10 mg/cm$^2$ (of tin) $Na_2SnO_3 \cdot 3H_2O$ for a source of gray tin. The abscissa gives absorber velocities relative to the source (the + sign corresponding to approach), while the ordinate gives the resonance absorption effect. From the curves, the halfwidths of the resonance peaks are 0.85 and 0.9 mm/sec respectively, which is sufficiently close to twice the natural line width 0.62 mm/sec, as found from the half-life of the first excited state $(1.85 \pm 0.1) \times 10^{-8}$ sec.[9] Within the limits of error, reducing the absorber thickness to 5 mg/cm$^2$ produced no noticeable change in the widths of the resonance lines.

There was a considerable broadening of the absorption curves for these same samples ($\beta$-Sn and $Na_2SnO_3 \cdot 3H_2O$) to values of 1.4—1.5 mm/sec when we used a source of $SnO_2$. Figure 2 shows the resonance absorption spectrum for 10 mg/cm$^2$ of $Na_2SnO_3 \cdot 3H_2O$. We note that there is no isomer shift between these compounds.

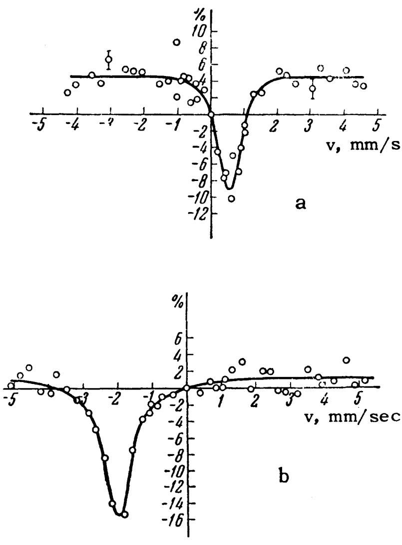

FIG. 1. Resonance absorption spectra in $\beta$-Sn (a) and $Na_2SnO_3 \cdot 3H_2O$ (b); the source was $\alpha$-Sn.

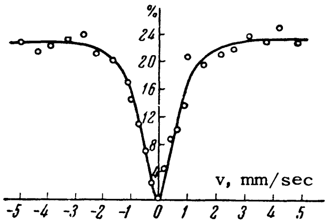

FIG. 2. Resonance absorbtion spectrum of $Na_2SnO_3 \cdot 3H_2O$; source was $SnO_2$.

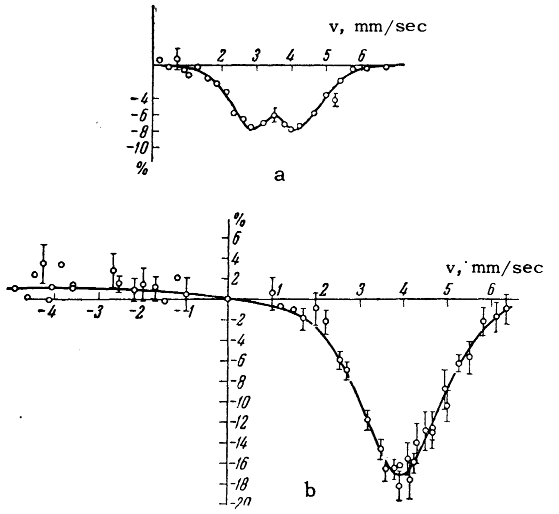

FIG. 3. Resonance absorption curves in (a) $SnCl_2 \cdot 2H_2O$, and (b) $SnSO_4$; the source was $SnO_2$.

The quadrupole interaction of the $Sn^{119}$ nucleus with the crystal lattice is seen clearly in the divalent tin compounds $SnCl_2 \cdot 2H_2O$ and $SnSO_4$, whose absorption spectra are shown in Fig. 3.[2] A study of the $SnSO_4$ absorber with the $\alpha$-tin source gave a narrower line with a definitely flat top. However, the absence of resolved peaks makes it difficult to determine the splitting accurately. For $SnCl_2 \cdot 2H_2O$, the value of $\Delta$ is $1.25 \pm 0.15$ mm/sec.

A very sizable Mössbauer effect was seen in compounds having a low melting point and containing light atoms. For example, in $SnCl_4 \cdot 5H_2O$ (40 mg/cm$^2$) the effect at the maximum was about 28%. The theoretical problems concerning the intensity of the Mössbauer line in the presence of impurity atoms have been treated by Yu. Kagan.[11-14]

The data on isomer shifts in various tin compounds relative to the transition in the $SnO_2$ source are given in the table (second column).

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[1] I.e., the counting rate as a function of the relative velocity of source and absorber.

[2] The resonance absorption effect in $SnCl_2 \cdot 2H_2O$ is relative to the counting rate at negative velocities.

| Compound | Shift, mm/sec | | |
|---|---|---|---|
| | Data from Physics Inst. Acad. of Sci. | Data of Moscow State Univ. | Data of Boyle et al [10] |
| $SnF_4$ | | | —0.44 |
| $SnO_2$ | 0 | $\leqslant$ 0.13 | —0.04 |
| $Na_2SnO_3\cdot 3H_2O$ | 0 | | |
| $SnBr_2$ | 0.20±0,05 | 0,20±0.09 | |
| $SnCl_4\cdot 5H_2O$ | 0.25±0.05 | 0.28±0.13 | 0.16 |
| $SnCl_4\cdot 2\{C_2H_4(NH_2)_2\}$* | 0.25±0.05 | | |
| $[SnCl_6]^{-2}\cdot 2\alpha$—An* | 0.40±0.10 | | |
| $(NH_4)_2SnCl_6$ | 0.50±0.10 | 0.42±0.19 | |
| $SnCl_4$ | 0,85±0.10 | | |
| $SnS_2$ | | 1.07±0.25 | 1,16 |
| $SnBr_4$ | 1.15±0.25 | | |
| $SnI_4$ | | 1.64±0.25 | 1.86 |
| α-Sn | 2.00±0.10 | | 2.06 |
| $SnNb_3$ | | 2.26±0.19 | |
| β-Sn | 2.55±0.15 | 2.77±0.25 | |
| SnO (tetrag.) | | 2.77±0.19 | 2.76 |
| $SnF_2$ | | 2.96±0.38 | 3.66 |
| SnS | | | 3.36 |
| $SnCl_2\cdot 2H_2O$ | 3.55±0.15 | | 4.76 |
| $SnCl_2$ | | 3.86±0.38 | 4.76 |
| $SnSO_4$ | 3.95+\|0.15 | | |

*Studied in collaboration with the laboratory of V. I. Gol'danskii (Institute of Chemical Physics).

## DISCUSSION OF RESULTS

From the experimental data we determined the probability f′ for resonance absorption of the $Sn^{119}$ γ quanta in different crystal structures. Two methods were used.

If the quadrupole splitting is absent or is small compared to the line width, one can find f′ uniquely from the ratio of the area of the curve to the value ε of the resonance absorption effect at the maximum. In such a calculation the resonance characteristic of the source, αf, is eliminated.

The limits of variation of the two unknown parameters f′ and αf were also determined from the intersection of the curves

$$\varepsilon = \alpha f\,[1 - I_0(a/2)\exp(-a/2)]$$

for several absorbers of different thickness. Here $I_0(a/2)$ is the Bessel function of zero order and imaginary argument, $a = \sigma_0 f' n$, $\sigma_0$ is the cross section at resonance, n is the number of nuclei of the resonance isotope per $cm^2$ of absorber.

At liquid nitrogen temperature the averaged values of f′ for β-Sn and $Na_2SnO_3\cdot 3H_2O$ found by the different methods were equal to 0.35 ± 0.07 and 0.56 ± 0.06 respectively. For the α-Sn source, the resonance parameter αf was 0.28 ± 0.03.

An estimate of the broadening of the emission spectrum of the α-source due to self-absorption showed that it cannot be increased by more than 0.05 mm/sec. No effect of distortion of the curves due to vibration was seen. Obviously these errors are within the limits of error of the measurements. Thus the observed broadenings of the absorption curves for β-Sn and $Na_2SnO_3\cdot 3H_2O$, for which the half-widths hardly changed with changing absorber thickness, can be explained as chiefly caused by a slight quadrupole splitting in these compounds.

Limits on the possible values of Δ for β-Sn are given in [8]: $0.19 \leq \Delta \leq 0.5$ mm/sec. According to our data the upper limit should be reduced to 0.35 mm/sec.

Considering these comments we may suggest that one should not attribute the broadening of the resonance spectrum in $Na_2SnO_3\cdot 3H_2O$ entirely to the effect of the finite absorber thickness, even if we include a slight difference in the probability f′ for β-Sn and $Na_2SnO_3\cdot 3H_2O$. Apparently there is a quadrupole splitting in sodium stannate, with an upper limit of 0.4 mm/sec.

The absence of an isomer shift between tin oxide and sodium stannate indicates an identical environment of the $Sn^{119}$ nucleus in these compounds. On the other hand, the substantial broadening of the spectrum to 1.4 mm/sec leads us to assume that there is also a splitting in $SnO_2$. An analysis of the data for $SnO_2$ absorbers (at room temperature and liquid nitrogen temperature) with sources of α-Sn and $SnO_2$ showed that the upper limit for Δ in $SnO_2$ is somewhat larger than the splitting in $Na_2SnO_3\cdot 3H_2O$.

Such a conclusion is in disagreement with the results of Shpinel', Bryukhanov and Delyagin[3,4] concerning the absence of quadrupole splitting for tin nuclei in the $SnO_2$ lattice. In this connection we should also mention that we did not obtain satisfactory agreement when we tried to fit the experimental half-widths for tin dioxide with an $SnO_2$

source (absorber and source at room temperature) to the curve $\Gamma_{exp} = f(n)$ given in [3]; when one makes the slight extrapolation to zero absorber thickness, one gets a value which is almost exactly twice the natural width of the excited state. An especially large difference is found for thin absorbers. For example, for a thickness of 5 mg/cm$^2$, $\Gamma_{exp} = 10 \times 10^{-8}$ eV, whereas the authors cited above give a value 30% lower.

The chemical shifts for the various tin compounds seem to be divisible into two subgroups corresponding to divalent and quadrivalent structures, except for the case of $SnBr_2$. Assuming purely ionic binding, one can get an approximate lower limit for the change $\Delta R/R$ in the effective radius of the nucleus in the excited state. Considering the outer electronic configuration of the tin atom ($5s^2 5p^2$) and assuming that the density of the 5s electrons at the nucleus is equal to zero in the quadrivalent compounds, one can determine a value $\Delta R/R \geq +0.8 \times 10^{-4}$ from the difference in the energy of the transitions in $SnO_2$ and $SnSO_4$.3) This quantity was determined to an accuracy of 30% in this same way in the work of Boyle et al.,[10] and was equal to $+1.1 \times 10^{-4}$.

In the third column of the table we give results of measurements by the group at the Nuclear Physics Institute of Moscow State University[4] 4) on energy shifts of the excited state in different tin compounds relative to the transition in $SnO_2$. We see that the results for a given absorber agree. The table also gives results found by Boyle et al.[10] Since these measurements were made with a $\beta$-Sn source, these data are referred to an intermediate value of the shifts for white tin, found by us in [4]. A point of interest is the large discrepancy, far outside the limits of experimental error, in the isomer shifts for $SnCl_2 \cdot 2H_2O$. In addition, for this material Boyle et al.[10] found no quadrupole splitting, whereas it appeared clearly in our measurements (cf. Fig. 3a). In later checks with $SnCl_2 \cdot 2H_2O$ absorbers prepared in different ways, we always found a well resolved splitting and a significantly smaller isomer shift.

It should be mentioned that the large difference in isomer shifts for $SnF_2$ and $SnCl_2$ found by the different authors [4, 10] is beyond the limits of error of the measurements.

## EXPERIMENTS WITH $Pr^{141}$

In addition to the experiments with tin, we attempted to detect the Mössbauer effect on $Pr^{141}$ nuclei. We investigated the $7/2^+ \rightarrow 5/2^+$ transition with an energy of 145 keV and a half-life of the excited state of $(2.0 \pm 0.3) \times 10^{-9}$ sec,[9] which corresponds to a value of 0.94 mm/sec for twice the natural width of the spectrum. The radiator was the radioactive isotope $Ce^{141}$ in the compound $CeO_2$. Cerium dioxide crystallizes in a cubic lattice, and so one should expect that there will be no quadrupole splitting of the line. But we know that all the rare earths and their compounds are strongly paramagnetic materials. Thus we cannot exclude a Zeeman splitting in both source and absorber. The absorber was the complex compound $Pr_2O_3 \cdot 4PrO_2$ ($\sim$900 mg/cm$^2$ of Pr).

Measurements of the absorption in the velocity interval ± 8 mm/sec showed no resonance effects within the limits of ±0.2%. Then an attempt was made to study this absorber by using scattering at 90°. The scatterer was at room temperature in this experiment. The ratio of the probabilities of transitions with different multipolarities, E2/M1, is $0.007 \pm 0.003$ for the 145-keV $\gamma$ transition, and the conversion coefficient is 0.3. The anisotropy of the angular distribution of resonance scattered $\gamma$ quanta, computed for a pure M1 transition, was not more than 20%.

Since in this last case we could not introduce collimation to eliminate differences in the geometrical conditions in recording when the absorber was at rest and when it was in motion, the results were referred to data for scattering from lanthanum oxide of approximately the same thickness. The scatterers were alternated during the course of the experiment. But here also no effect was seen within the limits of ± 1.5%.

In conclusion the author considers it a pleasant duty to express his sincere gratitude to F. L. Shapiro for his steady interest and considerable help in this work.

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3) The author reported the estimate of $\Delta R/R$ at the Conference on Nuclear Spectroscopy held in Leningrad in February, 1962.

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143