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CHEMICAL SHIFT OF THE K SERIES X RAYS OF TIN

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The shifts of the $K\alpha_1$, $K\alpha_2$ and $K\beta_1$ lines have been measured for Sn and SnO_2 using a Cauchois spectrometer with a scintillation detector, fitted with a device for alternately introducing sources for comparison. The results were $E^{Sn} - E^{SnO_2} = -0.19 \pm 0.01$ eV; -0.18 ± 0.02 eV; -0.22 ± 0.02 eV for $K\alpha_1$, $K\alpha_2$ and $K\beta_1$, respectively. The relative accuracy is 0.00006%. From the shift of the L_{III} level for Sn-SnO_2, which has been determined previously[1] to be -1.1 ± 0.3,[1] one can find the shifts relative to the Fermi level of the K, L_{II} and M_{III} levels to be -1.3 ± 0.3 eV, -1.1 ± 0.3 eV, and -1.1 ± 0.3 eV, respectively. The possibility of applying a similar method for observing isotopic and isomeric shifts of x-ray lines, and the effects associated with motion of the source and recoil in the emission or absorption of quanta is considered.

THE slight change in energy of the x-ray levels of an atom, occurring from the redistribution of density of valence electrons which takes place during formation of a chemical bond, has been called the chemical shift. This effect has been treated theoretically many times and observed experimentally.[1-4]

In recent years interest in the phenomenon of chemical shift has increased because of the possibility of using it to study the nature of chemical bonds and the whole complex picture of the mutual effects and deformability of electron shells. An additional inspiration was the successful use for similar purposes of the chemical shift of nuclear levels observed in the Mössbauer effect.[5-7]

Most studies of the chemical shift of x-ray lines have been carried out for emission lines using diffraction spectrometers.[3,4] The results obtained are for comparatively light elements (up to and including the iron transition group for the K series[3] and up to Pd for the L series[4]).

It seemed extremely promising to use the recently developed photoelectron method for studying the shift of x-ray levels.[1,8] But with this too one could not go beyond copper for the K-level shifts.[8] The L-level shifts were observed up to cadmium and tin[1].

This gap was partially filled by studies with the Mössbauer effect, which is, on the contrary, applicable only to comparatively heavy elements (heavier than iron). Unfortunately the number of isotopes with transitions suitable for practical work is very limited. Therefore the predominant part of the chemical work of this sort has been done with Fe^{57} and Sn^{119}.

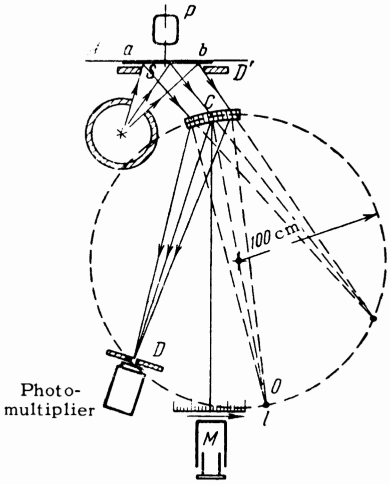

FIG. 1. Schematic diagram of the apparatus.

In analyzing the properties of Cauchois diffraction γ-ray spectrometers with scintillation recording,[9] we came to the conclusion that this apparatus may be extremely useful for observing small shifts of x-ray or γ-ray lines, in particular chemical shifts, and possibly isotopic and isomeric shifts of x-ray lines.

DESCRIPTION OF THE METHOD

The basic diagram of the equipment is shown in Fig. 1. The fluorescent radiation from a source S, excited by the primary radiation from an x-ray tube (15 mA, 200 kV) falls on the bent quartz single

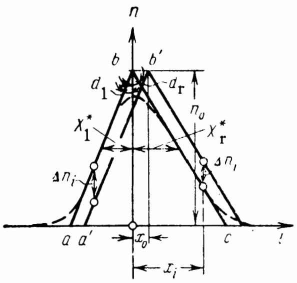

FIG. 2. Derivation of (1)-(3).

crystal C ($13\bar{4}0$ reflection planes normal to the large faces). The diffracted quanta are brought to a sharp focus (~ 0.05 mm for a γ line) at a distance of ~ 2 m from the crystal, and after passing through the receiving slit D which is 0.1 mm wide, are detected by a NaI(Tl) scintillation counter. The angle DCO between the detector and the reflection planes of the crystal is varied by means of lead screws moving the detector and the crystal, and is measured by the microscope M. (Each division of the scale of the counting equipment corresponds to 25 μ.)

The energy to which the equipment is tuned is determined by the angle DCO and, in first approximation, is independent of the position of the source S.

Consider (Fig. 2) a line obtained with such an equipment. Along the abscissa are marked the readings l on the microscope scale, while the ordinate gives the number of pulses recorded per counting interval. The shape of the line is roughly Gaussian, but in general somewhat asymmetric (with different widths at half maximum, X*, for the left and right halves). If we consider only the points on the steep sides, the profile can be approximated by the scalene triangle abc. Let a′b′c′ be the profile of the line from another source, like the first but displaced by an amount x_0 which is small compared to the line width. The shift x_0 is easily expressed in terms of the difference in counts $\Delta n^i = n_1^i - n_2^i$ from the first and second sources for a given position (x_0) of the equipment:*

$$x_0 = \Delta n_l{}^i \operatorname{tg} \alpha_l \quad \text{or} \quad x_0 = \Delta n_r{}^i \operatorname{tg} \alpha_r.$$

(the subscripts l and r indicate that they apply to the left or right half of the profile.) Since

$$\operatorname{tg} \alpha_l = 2X_l{}^* / n_0, \qquad \operatorname{tg} \alpha_r = 2X_r{}^* / n_0,$$

where n_0 is the altitude of the triangles,

$$x_0{}^i = 2\Delta n_l{}^i X_l{}^* / n_0 \quad \text{or} \quad x_0{}^i = 2\Delta n_r{}^i X_r{}^* / n_0. \tag{1}$$

An important point is that the value of the shift x_0 in this approximation is independent of the abscissas x^i of the points. To calculate the shift from the measured difference in counts Δn^i one need only know whether the particular point is to the right or left of the maximum.

If the differences Δn^i are measured for a series of points x^i, the required line shift x_0 can be found by taking a weighted average of the individual values:

$$\bar{x}_0 = 2\Sigma p^i \Delta n^i X^* / n_0 \Sigma p^i. \tag{2}$$

It is natural to take the weights p^i inversely proportional to the squares of the errors of the corresponding values of x_0^i. From (1) we have:

$$\delta^2 x_0{}^i = \delta^2(\Delta n^i) + \delta^2(n_0) + \delta^2(X^*);$$

n_0 and X* are determined by all the points of the profile, so that $\delta^2(n_0)$ and $\delta^2(X^*) \ll \delta^2(\Delta n^i)$, and

$$\delta^2(x_0{}^i) \approx \delta^2(\Delta n^i) \approx 2n^i / (\Delta n^i)^2.$$

Setting $p^i \sim (\Delta n^i)^2/n^i$, and using the relation $\Delta n_l^i X_l^* = \Delta n_r^i X_r^*$, we finally get

$$p^i_{l(r)} \sim 1/n^i X^{*2}_{l(r)}. \tag{3}$$

The treatment given here suggests the following measurement procedure. For each given position of the apparatus l^i, one takes the number of counts n_1^i when the first of the sources to be compared is in the field of view of the apparatus, and then without changing the position of the instrument one introduces the second source and measures n_2^i. The changing of sources is done automatically at one minute intervals determined by a timer. There is a simultaneous switching of the counting channels accumulating pulses from the first and second sources. After several switchings, assuring that one has accumulated enough counts in each channel, the accumulated numbers of pulses are recorded, the channels are cleared, and the apparatus is shifted to the next position (usually 25 μ on the microscope scale). In this way one successively takes the whole profile of the line.

The values of n_0 and X_l^*, X_r^* are determined graphically by drawing the lines, all later computations are done analytically using (2) and (3). In doing this one uses only points on the straight line portions of the sides (Fig. 2).

The line shape and width in spectrometers of this type are determined by the width of the entrance slit of the detector, by local aberration due to distortions of the reflecting planes of the bent crystal, and aperture aberration associated with

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*tg = tan.

Table I

$Sn_1 - Sn_2$ (K_{α_1})

$\bar{x}_0$, μ	$E^{Sn_1} - E^{Sn_2}$, eV
+0.97±0.56	−0.059±0.034
−0.40±0.83	+0.024±0.050
−0.48±0.49	+0.029±0.030
+0.40±0.54	−0.024±0.033
Average: +0.12±0.31(±0.35)	+0.007±0.019 (0.021)

the approximate nature of the focussing and with deviations from an ideal cylinder of the surface to which the crystal is bent.[9] Of all these factors only the aperture aberration causes a slight dependence of the shape (and position) of the line on the position of the source or the distribution of brightness of the radiation along the line ab of the source S (Fig. 1). (Variations of source brightness in the direction perpendicular to the plane of Fig. 1 are less important, since the apparatus does not focus in this direction.)

The sources were in the form of rather thick (~2 mm) plates with dimensions 30 × 130 mm. The plates were placed at opposite ends of an aluminum disk A (Fig. 1), which could be rotated through 180° about a horizontal axis by the motor P, between two extreme fixed positions, and introduced alternately into the field of view of the apparatus. The working area of the sources was determined by the fixed lead diaphragm D′ (with aperture 20 × 100 mm), placed right at the source so that it was precisely the same for both samples. We still had to check whether the presence of surface nonuniformities might lead to a different distribution of brightness along the line of the sources and thus, if aperture aberration was present, result in an aberrational shift of the lines to be compared.[1)]

A preliminary control experiment was done. It consisted in measuring the shift of the tin $K_{\alpha 1}$ line from two samples prepared from metallic tin. The counting rate at the maximum of the line was ~20,000 min^{-1}, the background ~400 min^{-1}. The full width at half maximum was ~300 μ (~18 eV). Table I gives the results of four series of measurements, in each of which ~40,000 pulses per channel were accumulated in the region of the maximum of the line. The errors given in col. 2 of Table I for the results of the different series are the mean squares found from the deviation from the weighted average (relation (2)) of the partial values x_0^i (relation (1)). For the results of the four series we calculated the internal mean square error in terms of the errors of the separate series, and the external error from the deviations from the common average of the results of the individual series (given in parentheses).

CHEMICAL SHIFTS OF K, L_{II} AND M_{III} LEVELS FOR $Sn-SnO_2$

The first choice for study was the pair Sn-SnO_2. The shift of the L_{III} level (relative to the Fermi level) is known for Sn-SnO_2 from the recent work of Nordling, using the photoelectron method.[1] One might therefore hope that measuring the shift of the $K_{\alpha 1}$ line, which corresponds to a transition between the L_{III} and K levels would enable one to determine the shift of the K level relative to the Fermi level; similarly, measurements of the other intense lines of the K series, $K_{\alpha 2}(L_{II} \rightarrow K)$ and $K_{\beta 1}(M_{III} \rightarrow K)$ should give the shifts relative to the Fermi level of the L_{II} and M_{III} levels.

An important fact is that there are data from the Mössbauer effect for the chemical shift between Sn and SnO_2.

One of the plates of the preceding experiment was used for the Sn sample. The SnO_2 sample was prepared by filling a rectangular cavity (3 × 30 × 130 mm) in a lucite plate with a heated carefully mixed paste of a fine powder of tin oxide with a little paraffin. After hardening, the surface of the sample was polished to coincide with the surface of the lucite plate. The sample was fixed on the disk of the sample changer at the place where the second tin plate was located in the preceding experiment.

The results of the experiments in three series for the $K_{\alpha 1}$ line are given in Table II (left). The intensities of the lines from Sn and SnO_2 differed by about 1%. Before treating the data, the SnO_2 was adjusted to the Sn line (using four or five points near the maximum). All the errors are mean square. As in Table I, the external errors are given in parentheses.

The preliminary experiment with surfaces ground to comparable accuracy showed that there is no effect of aberration. Nevertheless there was some question whether the different structure of the sources might result in the presence of aberration in the main experiment.

[1)] The most radical means for completely eliminating aberrational shifts would be to introduce the source in the form of a ring rotating in front of the diaphragm D′. But then there would be a marked increase in the material needed for preparation of the source. This is extremely undesirable, when we consider our plans for using the apparatus for studying isotope shifts (cf. below).

Table II

$Sn - SnO_2$ ($K_{\alpha 1}$)

Equipment in left position		Equipment in right position	
$\bar{x}_0$, μ	$E^{Sn} - E^{SnO_2}$, eV	$\bar{x}_0$, μ	$E^{Sn} - E^{SnO_2}$, eV
+3.28±0.50	−0.20±0.03	−2.77±0.59	−0.17±0.04
+3.27±0.55	−0.20±0.03	−3.13±0.38	−0.19±0.02
+4.31±0.48	−0.26±0.03	−2.75±0.69	−0.17±0.04
Average: +3.62±0.29(0.44)	−0.22±0.02 (0.03)	−2.88±0.33 (0.13)	−0.17±0.02 (0.01)

Table III

$Sn - SnO_2$ ($K_{\alpha 1}$) c with diaphragm

Equipment in left position		Equipment in right position	
$\bar{x}_0$, μ	$E^{Sn} - E^{SnO_2}$, eV	$\bar{x}_0$, μ	$E^{Sn} - E^{SnO_2}$, eV
+3.40±0.63	−0.21±0.04	−4.05±0.87	−0.24±0.05
+2.58±0.59	−0.16±0.04	−3.15±0.50	−0.19±0.03
+2.98±0.45	−0.18±0.03	−3.18±0.77	−0.19±0.05
—	—	−2.96±0.88	−0.18±0.05
Average: +2.99±0.32(0.24)	−0.18±0.02 (0.01)	−3.34±0.39 (0.25)	−0.20±0.02 (0.015)

To check this, control experiments were done. In the first control experiment, the working aperture of the bent crystal (horizontal) was reduced (by stopping) from 35 to 7.5 mm. This should significantly reduce the aperture aberration, and consequently the aberrational shift. The results of three series are shown at the left of Table III. Comparison with the data of Table II shows that the aberrational shift does not exceed 0.22—0.18 = 0.04 ± 0.03 eV.

The second control experiment consisted in repeating the preceding measurements in the symmetric right position of the diffraction spectrometer (cf.[9], p. 77).

If the shift is due to aberration, the appearance of the line will correspond to Fig. 3a. When we go from the right to the left position, the shift of the line along the scale *l* of the microscope keeps the same sign while the sign of the energy shift $E^{Sn} - E^{SnO_2}$ reverses. If the shift is caused by an actual difference in energy of the lines being compared, one gets the situation in Fig. 3b ($E^{Sn} - E^{SnO_2} < 0$ in both positions).

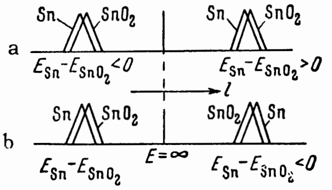

FIG. 3. Appearance of lines when working in the right and left symmetric positions of the apparatus: a – shift due to aberration, b – shift due to difference in energy of lines under comparison.

Comparison of the left and right halves of Table II shows that one has the situation corresponding to Fig. 3b, i.e., the observed shift is due mainly to a real difference in energy of the lines from Sn and SnO_2. Assuming that the possible aberrational shift is

$$\Delta E_r^{ab} + \Delta E_l^{ab} = 0.05 \pm 0.03 \text{ eV}$$

and remains constant in the left and right positions of the apparatus, half the sum of the right and left shifts should give the pure effect without the influence of aberration.

If, furthermore, the experiment with the diaphragm actually gives the pure effect without any influence of aberration, repetition in the right position (cf. Table III, right) should give the same result. This is actually the case:

$$\Delta E_r^d - \Delta E_l^d = 0.02 \pm 0.03 \text{ eV}.$$

Finally, half the sum of the effect for right and left in experiments with and without the diaphragm should coincide. Actually:

$$\overline{\Delta E}_{l\text{-}r} = -0.19_5 \pm 0.01_4 \text{ eV};$$

$$\overline{\Delta E}^d_{l\text{-}r} = -0.19_0 \pm 0.01_4 \text{ eV}.$$

The final result can be found as the average of all the experiments:

$$E^{Sn} - E^{SnO_2} = -0.19_2 \pm 0.01_0 \text{ eV}.$$

Table IV

$Sn - SnO_2\ (K_{\alpha 2})$

Equipment in left position		Equipment in right position	
$\overline{x_0}$, μ	$E^{Sn} - E^{SnO_2}$, eV	$\overline{x_0}$, μ	$E^{Sn} - E^{SnO_2}$, eV
+2.62±0.45	−0.16±0.03	−2.97±0.61	−0.18±0.04
+2.97±0.64	−0.18±0.04	−3.32±0.66	−0.20±0.04
+2.87±0.41	−0.17±0.02	−3.58±0.49	−0.21±0.03
Average: +2,82±0.30(0.11)	−0.17±0.02 (0.01)	−3.29±0.34 (0.18)	−0.20±0.02 (0.01)

Table V

$Sn - SnO_2\ (K_{\beta 1})$

Equipment in left position		Equipment in right position	
$\overline{x_0}$, μ	$E^{Sn} - E^{SnO_2}$, eV	$\overline{x_0}$, μ	$E^{Sn} - E^{SnO_2}$, eV
+2.87±0.81	−0.22±0.06	−3.28±0.56	−0.25±0.04
+2.68±0.59	−0.21±0.05	−2.05±0.57	−0.16±0.04
+4.07±0.63	−0.31±0.05	−2.03±0.63	−0.16±0.05
Average: +3.21±0.40 (0.44)	−0.25±0.03 (0,03)	−2.45±0.35 (0.42)	−0.19±0.03 (0.03)

The results of the measurements for the $K_{\alpha 2}$ and $K_{\beta 1}$ lines are given in Tables 4 and 5. During these experiments the crystal was not stopped down, and the average of the data from the right and left series was taken:

$$E^{Sn} - E^{SnO_2}\big|_{K_{\alpha 2}} = -0.18 \pm 0.02\ \text{eV},$$

$$E^{Sn} - E^{SnO_2}\big|_{K_{\beta 1}} = -0.22 \pm 0.02\ \text{eV}.$$

DISCUSSION OF RESULTS

The shifts of the K, L_{II} and M_{III} levels can be expressed in terms of the shift of the L_{III} level (relative to the Fermi level), which is known from the work of Nordling[1] ($\Delta E_{L_{III}} \equiv E^{Sn}_{L_{III}} - E^{SnO_2}_{L_{III}} = -1.1 \pm 0.3$ eV), and our data on the energy differences for the $K_{\alpha 1}$, $K_{\alpha 2}$ and $K_{\beta 1}$ lines:

$$\Delta E_K = \Delta E_{L_{III}} + \Delta E_{K_{\alpha 1}} = -1.3 \pm 0.3\ \text{eV},$$

$$\Delta F_{L_{II}} = \Delta E_{L_{II}} + \Delta E_{K_{\alpha 1}} - \Delta E_{K_{\alpha 2}} = -1.1 + 0.3\ \text{eV},$$

$$\Delta E_{M_{III}} = \Delta E_{L_{III}} + \Delta E_{K_{\alpha 1}} - \Delta E_{K_{\beta 1}} = -1.1 \pm 0.3\ \text{eV}.$$

The uncertainty is almost completely determined by the error in the value of $\Delta E_{L_{III}}$.[2)]

The chemical shift in the Mössbauer effect, which has also been measured for $Sn-SnO_2$,[5-7] is given by the formula

$$\Delta E \sim \frac{\Delta R}{R}\left[\Psi_S^2(0)^{Sn} - \Psi_S^2(0)^{SnO_2}\right],$$

where ΔR/R is the percentage change in the charge radius of the nucleus in going from the excited to the ground state, $\Psi_S^2(0)^{Sn}$, $\Psi_S^2(0)^{SnO_2}$ are the S electron densities at the nucleus for Sn and SnO_2 respectively.

The $Sn-SnO_2$ system may thus be very useful for testing our notions about mutual screening and deformability of electron shells, and may enable us to compare theory and experiment on several points.

An interesting consequence of such a check for nuclear physics might be improvement in the value of ΔR/R for the tin nucleus.

Using the relation between the relative accuracy and the energy of the line which is characteristic of diffraction equipment:[9]

$$\delta E / E = \beta E, \tag{5}$$

where δE is the absolute error in determining the energy shift, β is a constant, and taking the experimental values of δE found from the experiments with tin, we estimate the ability of our instrument to detect small shifts of x-ray (or γ) lines with different energies. Setting δE = ± 0.015 eV, E ($K_{\alpha 1}$, Sn) = 2.53×10^4 eV, we find for the experiment with tin, $\delta E/E = 6 \times 10^{-7}$ (± 0.00006%). Relation (5) becomes

$$\delta E / E = 2.4 \cdot 10^{-8}\, E\ (\text{keV}). \tag{5'}$$

[2)] The minus sign on the level shifts means that the distance between the corresponding level and the Fermi level is smaller in Sn than in SnO_2.

Table VI

	Theory	Results of earlier work		Results expected using this method	
		Effect observed	Results	Effect observable	Expected result
Chemical shift (K series)	$Z\leqslant29$; $\Delta E\approx1$eV $Z>29$; $\Delta E\approx0.1$— —1eV	yes no	1—4eV* [3,8] —	— yes	— 0.01 $(Z\approx40)\leqslant\delta E$ $\leqslant0.1$eV $(Z\approx80)$
Isotope shift	$\Delta E\approx0.034$eV $\Delta E\approx0.40$eV $\Delta E\approx0.018$eV** [10]	no — no	$\delta E=\pm0.2$eV — $\delta E=\pm0.4$eV [11]	yes — yes	$\delta E\approx\pm0.01$eV
Isomer shift	$\Delta E\approx0.01\div0.1$eV[12] $\Delta E\approx0.1$eV*** [13]	— no	— $\delta E=\pm0.7$eV[13]	— yes?	— $\delta E\approx\pm0.06$eV
Doppler shift from source motion	$\Delta E/E=v/c$	yes; Mössbauer effect		yes	For $E\approx2.5\cdot10^4$eV and $\Delta E=\delta E\approx0.015$eV $v=180$ m/sec
Doppler shift from recoil in emission of quantum	$\Delta E/E=E/2Mc^2$	yes; Mössbauer effect		no	For $A=100$ $\Delta E/E$ $=0.53\cdot10^{-8}E$ (keV) $\delta E/E=2.4\cdot10^{-8}E$(keV)
Doppler shift from preceding recoil	$\Delta E\approx EE'/Mc^2$ $E\ll E'$	—	—	yes	For $A=100$ with $\Delta E=\delta E$ $E'\approx2.3E$

Note. The symbol ΔE gives the magnitude of the effect, and δE the absolute error in the observation of the effect.

*Uncertainty ± 1 − 0.05 eV

**These are for the levels $1s_{1/2}$ Mo$^{92-100}$, $2s_{1/2}$ U$^{235-238}$ and $2p_{1/2}$ U$^{235-238}$, respectively.

***For the $K_{\alpha1}$ line of Tm^{169}.

Table VI gives the theoretical estimates of certain effects related to small shifts of x-ray (or γ) lines, the results of earlier experiments, and an estimate of the possibility of applying the proposed method.

The comparison shows that the method described above can undoubtedly be useful for systematic investigations of chemical shifts of x-ray levels (including K levels) in the range $40 \lesssim Z \lesssim 80$. Possibly by using it one may be able to observe isotopic and isomeric shifts of x-ray lines.

The Doppler shift associated with motion of the source can be observed with quite moderate source velocities. Measurement of the shift caused by recoil during emission of a γ quantum (or x-ray) offers the attractive possibility of determining the recoilless fraction (as in the Mössbauer effect) for all transitions of suitable energy. But to observe this effect one must increase the accuracy by approximately an order of magnitude. On the other hand, with the present accuracy one can already measure the shift caused by recoil in any preceding emission process. Thus, in the measurement of the shift of the $K\alpha_1$ line of Sn, one can feel a recoil equivalent to that which occurs in the absorption of a quantum with energy ~ 60 keV.

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