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THE CHEMICAL SHIFT DUE TO THE SCREENING OF THE INNER LEVELS OF HEAVY ELEMENTS

O. I. SUMBAEV, A. F. MEZENTSEV, V. I. MARUSHENKO, E. V. PETROVICH, and A. S. RYL'NIKOV

A. F. Ioffe Physico-technical Institute, Academy of Sciences, U.S.S.R.

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The chemical shifts of the Kα_1 x-ray lines of Mo–MoO$_3$, Sn–SnO$_2$, and W–WO$_3$ are measured by a method based on alternately introducing the compared sources into the field of view of a Cauchois diffraction spectrometer with compensated aperture aberration. The energy differences E(Kα_1) for the metal and oxide are respectively $+192 \pm 7$, -152 ± 5, and $+110 \pm 33$ meV.* Thus the result we previously obtained for Sn–SnO$_2$[12] has now been confirmed on an improved experimental setup. It is shown that despite the commonly accepted viewpoint,[1] the inner (K, L) atomic level shifts due to chemical bond formation are appreciable up to the heaviest elements, and moreover their absolute value remains approximately constant with increasing Z. This conclusion is in agreement with the theoretical estimates made by us on the assumption that the chemical effects observed are due to internal screening.[7, 8] It is noted that the effect can be used for investigating the nature of the chemical bond as was done previously in the case of light elements.

INTRODUCTION

CHANGES in the energy of x-ray emission lines or of the absorption edges due to chemical transformations are well-known phenomena which have been investigated for several decades (see, for example, [1, 2] Nevertheless, there is some lack of clarity in the treatment of these effects.

Generally attention is paid above all to changes in the energy of the outer (valence) electrons occurring in the formation of the chemical bond and to the corresponding rearrangement of the crystal bands. It is further assumed that the attendant perturbations of the inner shells attenuate rapidly as one passes deeper into the atom.[1]

Effects such as the chemical shifts of the absorption edges, the chemical shifts of the outermost (hardest) lines of the x-ray emission series, chemical shifts of the distances between the inner levels of the atom and the Fermi level,[3, 4] are a measure of the change in the distance between one of the inner levels and the zone of the location of the outermost electrons. It is always possible to consider the observed chemical shift to be due to a shift of the outer level.

It would seem that investigations of the chemical shift of the softest emission lines of the K and L series corresponding to transitions between inner levels could furnish information on the chemical shifts of inner levels. A rather large amount of experimental data of this type is available (see, for example, [1, 2, 5, 6]). The analysis of these data indicates that the shift of a given level can only be followed up to some definite value of Z, i.e., it is quite noticeable in experiments with light elements, and gradually stops being noticeable within experimental accuracy on going over to heavy elements. This circumstance, together with the above point of view with regard to the effect, led to the view that the chemical shifts of the inner levels decrease on going over to the heavier elements of the periodic table, and made it even possible to indicate definite limits of Z values, above which the shifts of the given levels are negligibly small and experimentally unobservable. It is thus asserted that the shift of the L$_{\text{II}}$ and L$_{\text{III}}$ levels should not be observed for $Z > 26$, M$_{\text{I}}$ for $Z > 29$, M$_{\text{II-III}}$ for $Z > 32$, etc.[1]

The measurements were carried out with the aid of diffraction spectrometers, a general property of which is the quadratic decrease of the dispersion with the energy of the investigated line:

$$dl / dE = cE^{-2}, \tag{1}$$

where dl is the linear distance on the focusing circle between lines with energy in the range of E

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*The authors use a unit 1 meV = 10^{-3} eV (not to be confused with the 1 MeV = 10^{6} eV) – Tr.

separated by an energy interval dE. Since $E \sim Z^2$ (Moseley's law)

$$dl\,/\,dE \sim Z^{-4}. \tag{1'}$$

Therefore the experimental "disappearance" of the effect with increasing Z would also occur if its absolute value were constant. Furthermore, a mechanism is known, allowance for which would apparently indicate that the assertion regarding the rapid decrease of the chemical shift as one proceeds deeper into the atom may turn out to be incorrect. The valence electron screens the inner electrons; therefore the rearrangement of the valence-electron density in forming a chemical bond should lead to a change in the degree of screening of inner shells and to a shift in their energy. As far as we know, the first to consider such an effect in connection with the shift of x-ray levels was Karal'nik.[7, 8]

Let P be the probability of finding a valence electron closer to the nucleus than an electron of the inner shell whose screening is being considered. For s electrons P can be simply expressed in terms of radial wave functions:[9]

$$P = \int_0^\infty R_{ns}(r_1)\left[\int_0^{r_1} R_{n's}(r)\,dr\right]dr_1, \tag{2}$$

where $R_{ns}(r)$ and $R_{n's}(r)$ are the probabilities of finding an electron in a spherical shell of unit thickness and radius r for one of the inner electrons (whose screening is being considered) and of the valence electron respectively. If $E_{nsZ} - E_{nsZ-1}$ is the energy difference of the ns levels of elements Z and Z − 1, corresponding obviously to the shift for complete screening of one elementary charge, then the decrease in the binding energy of the level due to one valence electron for a screening P will be given by the relation:[8]

$$\Delta E_{ns} = (E_{nsZ} - E_{nsZ-1})P. \tag{3}$$

Using the values of P for a mercury atom, calculated in [9] on the basis of data of Hartree[10] for R_{ns}, and tabulated differences $E_{nsZ} - E_{nsZ-1}$, one can estimate the energy shifts of the K, L_I, and M_I levels of an isolated mercury atom which will occur on complete removal of one valence s electron:

$$\Delta E_K = 2393 \cdot 2.034 \cdot 10^{-5} \approx 0.05\ \text{eV},$$
$$\Delta E_{L_I} = 409 \cdot 1.912 \cdot 10^{-4} \approx 0.08\ \text{eV},$$
$$\Delta E_{M_I} = 140 \cdot 9.010 \cdot 10^{-4} \approx 0.13\ \text{eV}.$$

It is seen that the shift is appreciable even for the K level of an atom with Z = 80; furthermore, the absolute value of the shift changes little on going over from the M_I level ($E \approx 3.5$ keV) to the K level ($E \sim 83$ keV). In actual chemical compounds the valence may on the average amount to 3–4 units, and the degree of ionicity may be of the order of 0.5. These estimates indicate thus that one should expect a chemical screening shift of the order of 0.1 eV even for the K levels of the heaviest elements. Values of similar order of magnitude are obtained for the differences $\Delta E_K - \Delta_L$, $\Delta E_K - \Delta E_M$, i.e., for the chemical shift of the emission lines.

The values cited are of course estimates. They allow only for the direct effect of the removal of the valence s-electron on the considered inner shell and no attention is paid to the deformations of other shells which, arising during such a removal, affect in turn the investigated shell. In other words, although the initial functions of the neutral atom are indeed self-consistent, the wave functions of the ion are not self-consistent. In addition the estimates were made within the framework of the Hartree method, i.e., without allowance for the exchange interaction between the shell which can in this type of problem turn out to be appreciable. Finally, of course, only the case of removal of an s electron has been considered. Other (p and d) electrons may also participate in the chemical bonding, the fact that they are "drawn away" giving rise to shifts that differ both in magnitude and sign (see, for example, [8, 11])

The present variant of the method of measuring small energy shifts of x-ray and gamma lines worked out in our laboratory[12, 13] makes it possible to measure shifts whose relative magnitude is given by the relation

$$\delta E\,/\,E = (1 - 1.2) \cdot 10^{-8}\ E(\text{keV}), \tag{4}$$

where E is an energy of the order of the energy of the investigated line. It appears possible to follow a shift of the order of 0.1 eV up to energies of 70–100 keV, i.e., up to the emission lines of the K series of the heaviest elements, and to clarify the real variation of the chemical shift with Z.

An important consideration stimulating these measurements was also the hope that the screening effect of the chemical shift of the x-ray emission lines due to transitions between inner levels could become a useful method of investigating the nature of the chemical bond of a broad class of elements and their compounds.

As concrete objects of measurement we chose the $K\alpha_1$ (L_{III}–K) lines of Mo–MoO_3 (Z = 42), Sn–SnO_2 (Z = 50), and W–WO_3 (Z = 74).

To solve the problems of this paper one could of course have chosen any elements with similar

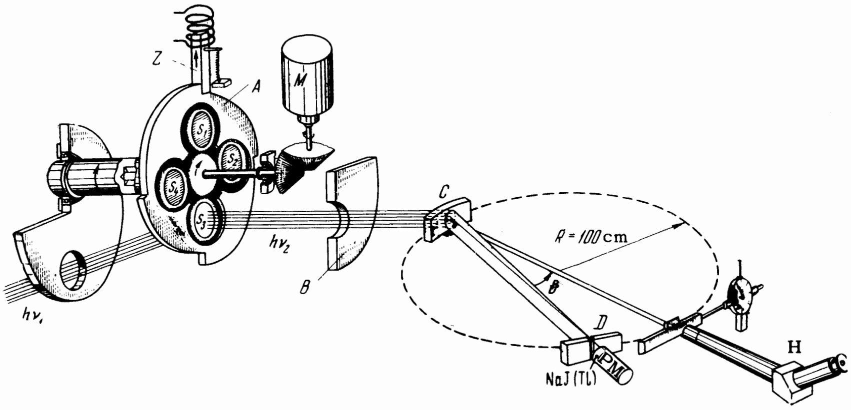

FIG. 1. Schematic diagram illustrating the principle of the apparatus. $S_1 - S_2$ – compared samples (sources), A – disc holder of the sources, Z – adjustable plunger for placing the investigated sample into the field of view of the instrument, M – motor for rotation and change of samples, B – defining diaphragm, C – bent crystal with driving lever, D – receiving slit of the scintillation detector, and T and H – the micrometer and the microscope for reading off the angle of rotation of the crystal.

values of Z, which were convenient from the experimental point of view. The choice of the $K\alpha_1$ lines of Mo and W is connected with their proposed use as standards for determining the X unit.[14-16] It is proposed to use Mo and W directly as the anodes. It is known, however, (see, for example, [1]) that the anode material may undergo chemical transformations in the course of operation (formation of oxides and carbides). It seemed, therefore, important to measure for these elements the magnitude of the chemical shifts which, if they appeared during the use of the standard emitters, would lead to instability of the standards.

Measurement of the chemical shift of the $K\alpha_1$ line of $Sn{-}SnO_2$ was the first application of our method,[12] and it seemed important to check this result by repeating the measurements on a new, more refined version of the experimental setup.

DETAILS OF THE EXPERIMENT AND RESULTS

The preliminary versions of the experimental setup which were used previously in investigations of the chemical shift of the K series x-ray lines of tin[12] and also of the isotopic shift of the $K\alpha_1$ line of the isotopes of molybdenum[13] have been described in the corresponding papers. Improvements of the setup have gradually been made. Thus, whereas the first measurements of the chemical shift in $Sn{-}SnO_2$ were carried out by reflection from large nonrotating samples, in studying the isotope shift we used transmission through small samples; the samples were rotated to compensate for aberrational shifts. The same version of the setup ([13], Fig. 1) was also used in the majority of measurements described in this paper. An exception is only the repeated experiment on the chemical shift in $W{-}WO_3$ (see below) for which we used an even somewhat more refined variant.

The schematic diagram of this variant is shown in Fig. 1. The difference between this and the previous setup consists in the use of four, and not as previously two, continuously rotating samples which are in turn introduced in the field of view of the device. The advantage of such a construction, in addition to an increase in the number of simultaneously compared samples is the complete symmetry of the setup in all four compared positions.

All samples which were used in the measurements in this paper were in the form of discs 13 mm in diameter; the thicknesses of 50, 75, and 175 mg/cm^2 for Mo, Sn, and W respectively insured maximum counting rates at the lines (see Fig. 2). The MoO_3, SnO_2, and WO_3 samples were prepared from commercially pure oxides in a mold under a pressure of 4000 atm; 100–200 mg of teflon powder was first carefully mixed in with the finely powdered oxide. The metallic molybdenum and tungsten samples were cut from commercial foil of appropriate thickness. The tin samples were pressed in a mold from previously suspended reguli of pure metallic tin.

The counting rates at the line maxima were 8000, 40,000, and 10,000 min^{-1} respectively for $Mo{-}MoO_3$, $Sn{-}SnO_2$, and $W{-}WO_3$; the background was 100, 700, and 2000 min^{-1}. The line widths on

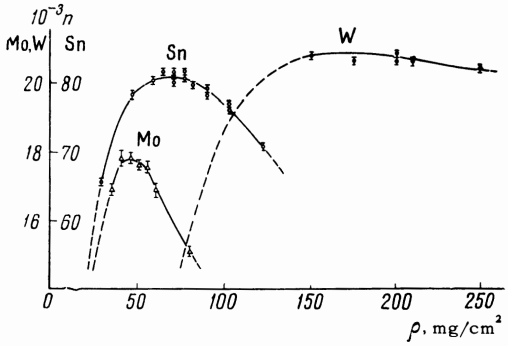

FIG. 2. Dependence of the intensities of the K_{α_1} lines of molybdenum, tin, and tungsten on the thickness of the sources.

the focusing circle (at half height) were ~300 μ, the reciprocal dispersions being 0.0291, 0.0606, and 0.335 eV/μ respectively for molybdenum, tin, and tungsten; the line widths in electron volts were 9, 18, and 100.

Tables I–IV list the results of the different measurement series. Each series consisted of 14–18 double (or, as in the main W–WO_3 experiment, fourfold) points, 2″ in the angle ϑ. The total time of gathering information from each source was 2 minutes per point. The errors in the values cited in Tables I–IV are the external mean-square errors calculated from the deviations of the results of the separate series from the general mean.

In the Mo–MoO_3 experiment (Table I) we used several samples of Mo and MoO_3 in order to convince ourselves that there was no aberrational shift due to the inhomogeneity of the samples. For the same reason a part of the measurements were carried out in the left-hand symmetrical position of the spectrometer (see [12]). The final result is taken to be the average value of all series:[1)]

$$E^{\mathrm{Mo}} - E^{\mathrm{MoO_3}} = +192 \pm 7 \text{ meV}.$$

The result of the experiment with Sn–SnO_2 (Table II) is:

$$E^{\mathrm{Sn}} - E^{\mathrm{SnO_2}} = -152 \pm 5 \text{ meV}.$$

The chemical shift in Sn–SnO_2 was measured in our first work using the Cauchois spectrometer method with interchange of the compared samples,[12] and we obtained

$$E^{\mathrm{Sn}} - E^{\mathrm{SnO_2}} = -192 \pm 10 \text{ meV}.$$

The discrepancy of 40 ± 11 meV is outside the limits of statistical errors. The reason for the discrepancy may be an incomplete exclusion of the aberrational shift in the first experiment in which large nonrotating samples were used.

Table I. The chemical shift of the $K\alpha_1$ line of Mo–MoO_3

Series No.	$E^{\mathrm{Mo}} - E^{\mathrm{MoO_3}}$ (meV)
1	210 ± 19
2	206 ± 22
3	212 ± 15
4	220 ± 15
5	230 ± 18
6	198 ± 20
7	155 ± 19
8	190 ± 22
9	183 ± 24
10	199 ± 24
11	169 ± 13
12	153 ± 24
13	173 ± 12
Average	192 ± 7

Note. Series 1 – 4 were obtained with sample No. 1 of Mo and sample No. 1 of MoO_3; series 5 and 6 – with No. 2 and No. 2; series 7 – 10 with No. 2 and No. 3; series 11 – 13 with No. 2 and No. 4; series 1 – 10 were obtained in the left-hand symmetrical spectrometer position, the series 11 – 13 – in the right-hand position.

Table II. The chemical shift of the $K\alpha_1$ line in Sn–SnO_2

Series No.	$E^{\mathrm{Sn}} - E^{\mathrm{SnO_2}}$ (meV)
1	$--147 \pm 21$
2	$--141 \pm 21$
3	$--160 \pm 16$
4	$--175 \pm 16$
5	$--145 \pm 19$
6	$--157 \pm 14$
7	$--150 \pm 20$
8	$--144 \pm 24$
Average	-152 ± 5

The experiment on the chemical shift in W–WO_3 was repeated twice. In the first version (see Table III) two metallic tungsten samples were first compared with each other, viz., W^{I}–W^{II}, then one of these samples was compared with an oxide sample, viz., WO_3^{I}–W^{I}, then W^{II}–WO_3^{II}, and finally WO_3^{I}–WO_3^{II}. The sharp decrease in the dispersion of the diffraction spectrometer with the atomic number of the investigated elements (see Introduction) leads to the circumstance that a linear shift of only 0.3μ corresponds to the measured effect ~0.1 eV. Such a shift is comparable with the spurious effect of the shift due to the elastic aftereffect in the rotation mechanism of the crystal (see [13]). The magnitude of the spurious shift can be estimated from the values obtained in the experiments with W^{I}-W^{II} and WO_3^{I}–WO_3^{II} which are somewhat outside the error limits.

In order to exclude any influence of the elastic aftereffect on the final result, the positions of the metal and oxide samples in the sample-holder windows were switched when WO_3^{I}–W^{I} was replaced by W^{II}–WO_3^{II} after the first six series of measurements. Thus, whereas in measuring WO_3^{I}–W^{I} the sequence began with the placing of WO_3 in the field of view of the instrument, in the experiment with W^{II}–W_3^{II} the metal sample was first. Therefore, whereas in the WO_3^{I}–W^{I} experiment the shift due to the elastic aftereffect was subtracted from the effect, in the W^{II}–WO_3^{II} experiment it was added to it.

[1)] It should be emphasized that all the cited errors are mean-square errors, i.e., they take into account only statistical deviations. In addition, the results can include systematic errors which we estimate to be about 10% of the magnitude of the effects.

Table III. The chemical shift of the $K\alpha_1$ line in W–WO_3 (preliminary experiment)

Series No.	$\Delta E^{W^I-W^{II}}$ (meV)	$\Delta E_I^{WO_3{}^I-W^I}$ (meV)	$\Delta E_{II}^{W^{II}-WO_3{}^{II}}$ (meV)	$\frac{\Delta E_I+\Delta E_{II}}{2}$	Weight	$\Delta E^{WO_3{}^I-WO_3{}^{II}}$ (meV)
1	− 70±150	+190±180	+310±180	+250	1	−100±210
2	+140±120	−260±150	+240±180	− 10	1	+240±110
3	+330±150	+280±140	+100±200	+190	1	− 20±130
4	+480±170	− 90±130	+130±150	+ 20	1	+180±190
5	−160±220	−100±200	+540±220	+220	1	−210±170
6		+130±310	−150±170	− 10	1	
Average	+140±120	+25±80	+200±90	+110±50		+20±80

The average value of the i-th series with WO_3^I–W^I and the i-th series with W^{II}–WO_3^{II}, cited in column 5 of Table III, require no corrections for the zero shift due to the elastic aftereffect. The averages of all these values were accepted as the final result of the experiment:

$$E^W - E^{WO_3} = +110 \pm 50 \text{ meV}.$$

The mean-square error of the result was obtained from the deviations of the average values of column 5 of Table III from the average.

In order to check and refine this result, the experiment was repeated on the improved version of the setup (Fig. 1). In order to decrease the shift of the zero due to the elastic aftereffect we increased the time between the instant the instrument was set in a new position in the angle ϑ and the instant at which accumulation of counts began from 30 sec to 2 min, and doubled the frequency of changing the samples. By combining measurements of different pairs of sources in a single series, it was possible to decrease considerably the effect of the residual shift on the result of the series. In the sequence WO_3^I–W^I–WO_3^{II}–W^{II} such a combination which excludes the influence of the aftereffect can be chosen in the form

$$E^W - E^{WO_3} = \frac{1}{2}\left[\frac{(E^{W^I} - E^{WO_3{}^I}) + (E^{W^I} - E^{WO_3{}^{II}})}{2} + \frac{(E^{W^I} - E^{WO_3{}^{II}}) + (E^{W^{II}} - E^{WO_3{}^{II}})}{2}\right].$$

The data from the individual series combined according to this relation are given in Table IV.

Table IV. The chemical shift of the $K\alpha_1$ line in W–WO_3 (main experiment)

Series No.	$E^W - E^{WO_3}$ (meV)	Weight	Series No.	$E^W - E^{WO_3}$ (meV)	Weight
1	+10	1	6	−150	1
2	+170	1	7	+50	1
3	+110	1	8	+160	1
4	+230	1	9	−40	1
5	+270	1	10	+280	1
			Average	+110±45	

The result of the repeated experiment

$$E^W - E^{WO_3} = +110 \pm 45 \text{ meV}$$

is in good agreement with the result of the preliminary experiment.

The final value of the chemical shift of the $K\alpha_1$ line of W–WO_3 was taken to be the weighted mean of the preliminary and repeated experiment:

$$E^W - E^{WO_3} = +110 \pm 33 \text{ meV}$$

(see footnote $^{1)}$). Equal weights were given to the data of column 5 (Table III) of the preliminary experiment and to the data of the individual series of the main experiment (Table IV). The mean-square error of the summary result is indicated.

In the case of Mo–MoO_3 and Sn–SnO_2 the effects are sufficiently large compared to the errors of the individual series, and in particular compared with the statistical errors of the results. For this

Table V. Pearson's agreement criteria and confidence intervals for the data of experiments with W–WO_3

Preliminary experiment			Repeated experiment		
Series No.	$x_i - \bar{x}$	$\left(\frac{x_i - \bar{x}}{\sigma_i}\right)^2$	Series No.	$x_i - \bar{x}$	$\left(\frac{x_i - \bar{x}}{\sigma_i}\right)^2$
1	+140	1.08	1	−100	0.44
2	−120	0.79	2	+ 60	0.16
3	+ 80	0.35	3	0	0.00
4	− 90	0.45	4	+120	0.63
5	+110	0.67	5	+160	1.12
6	−120	0.79	6	−260	2.96
		4.13	7	− 60	0.16
			8	+ 50	0.11
			9	−150	0.99
			10	+170	1.27
					7.84
$\sigma_i = \frac{190}{\sqrt{2}} = 135$ meV, $P(\chi^2) = 0{,}4$			$\sigma_i = \frac{\sqrt{10}}{4} \cdot 190 = 151$ meV, $P(\chi^2) = 0.5$		

$$\tilde{S} = \left(\frac{1}{n}\sum(x_i - \bar{x})^2\right)^{1/2} = 126 \text{ meV}$$

Note. x_i and $\bar{x}$ are the current and average values of the measurements from Tables III and IV; σ_i is the mean-square error of the result of a series; $P(\chi^2)$ – Pearson,s agreement criteria; $\tilde{S}$ – mean-square deviation of the result of one series from the common average of the combined data of the preliminary and repeated experiment.

reason the statistical reliability of these data is obvious. This is not so in the case of the experiments with W–WO_3. Here the errors of the individual series exceed somewhat the effect and even the statistical reliability of the final result requires more detailed comments.

Table V lists the results of the calculations of Pearson's agreement criteria for the preliminary and repeated experiments and the confidence intervals according to Student. Here σ_i are the errors of the preliminary experiment (the errors of the values from column 5 of Table III) and of the results of the individual series of the repeated experiment. We calculated them starting from the experimental mean value of the internal error for $E_i^W - E_i^{WO_3}$ which was ± 190 meV. $P(\chi^2) = 0.4$ and 0.5 are the Pearson criteria for the preliminary and repeated experiment indicating that the experiments are unsorted as regards the scatter of the values of the individual series, i.e., in approximately 40–50 out of 100 analogous experiments the scatter of values will be greater than in the given experiment, and in 60–50 experiments it will be smaller.

The confidence intervals calculated for the common average of both experiments allows one to state with a 90% reliability that the true value of the chemical shift for W–WO_3 is bracketed by the limits

$$50\,\text{meV} \leqslant (E^W - E^{WO_3}) \leqslant 170\,\text{meV},$$

i.e., it corresponds with a reliability of 90% to a magnitude of ~0.1 eV expected on the basis of estimates from the screening mechanism.

The very presence of the effect and its sign have been established by these experiments with a reliability of 99%, which corresponds to the interval

$$15\,\text{meV} \leqslant (E^W - E^{WO_3}) \leqslant 200\,\text{meV}.$$

DISCUSSION OF RESULTS

The data cited above show that the chemical shift of x-ray lines due to transitions between the innermost levels of the atom are experimentally observed up to the heavy elements of the periodic table. The absolute value of the chemical shift remains approximately constant in a broad range of atomic numbers of the elements.

This constancy and the very presence of a chemical shift of the $K\alpha_1$ line in the case of an element as heavy as tungsten, coinciding in magnitude with estimates based on the screening mechanism, makes it likely that the screening is the main effect responsible for the chemical shift of the inner levels in heavy atoms.

If this is the case, then there appears the possibility of using measurements of the chemical shifts between inner levels to obtain quantitative information about the chemical bonding by employing the following scheme: the shifts of the inner levels of a free atom with the valence electrons completely removed or excited to a given excitation are calculated on the basis of results of Hartree-Fock calculations (in analogy with the procedure followed, for example, in [17]); the same quantity is measured experimentally; a comparison makes it possible to obtain an equation for the degree of ionicity or to determine one of the parameters characterizing the bond in the investigated compound.

Approximately the same scheme based on a treatment of the shifts as the result of inner screening, was employed in a study of chemical bonds of lighter atoms using the chemical shift of the x-ray levels (see, for example, [11, 18, 19]). In the case of the inner levels of heavy atoms it is all the more justified, since the influence of band effects on the inner levels of heavy atoms is apparently negligibly small (in any case it is smaller than for comparatively light atoms).

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