Mechanisms for K X-ray Energy Shifts

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A detailed study of the energies of K x-ray transitions in dependence on the excitation mechanism is reported. Using high resolution focussing crystal spectrometers, small energy shifts could be detected the origin of which is attributed to different effects. The agreement between calculation and experiment strongly supports the given interpretation.

1. Introduction

The energies of K x-rays are known to be characteristic for a given element irrespective of the excitation mechnism. By advanced experimental methodes, however, minute energy shifts became visible that give new insight in nuclear and atomic properties and elucidate the processes involved. Since 15 years x-ray energy shifts are known that originate in the finite size of the nucleus and in the change of electronic screening due to the chemical bond [1 – 14].

More recently, three other effects were found that shift the x-ray energy in the order of 10^{-3} to 10^{-4} of the natural line width [15 – 25]. The conservation of the total angular momentum of the atom in electron capture β-decay (EC) and internal conversion processes (IC) leads to a non-statistical population of the hyperfine components that causes a shift of the compound line [10, 13, 15, 20]. The different probabilities for multi-hole creation in various excitation mechanisms lead to different satellite structures of the corresponding complex x-ray lines thus shifting the center of gravity [19, 20, 22 – 25]. Due to the short life time of the K-hole, in the EC β-decay the mother's atomic configuration may still exist when the characteristic x-ray is emitted. So, especially when additional inner shell electrons are present (4f, 5d, 5f), the K-shell transitions exhibit a characteristic shift pattern [17, 18, 20].

As a natural extension of these experiments the influence of excitation mechanism and chemical bond on the intensity of K x-rays has been investigated. These studies revealed significant intensity shifts for the K0-transitions depending on the chemical configuration [26 – 28]. In the course of these experiments the behaviour of absorption in the vicinity of the K-edge was carefully investigated. These effects could be shown to cause a significant energy shift of the K0 transition [29]. In the light of these findings the results of the systematical study of 4f, 4d, and 5d elements [15 – 20] will be discussed and compared with theoretical calculations.

2. The Experimental Method

Due to the smallness of the effects only high resolution crystal spectrometers could be used which have been described elsewhere [25, 30, 37]. To push the performance further a special twin source technique has been developed that allows a quasi-simultaneous measurement of two separate sources at a time [25, 28]. Thus the energy shifts have always been obtained through measurements with pairs of sources. In this way an ultimate accuracy of about 10^{-6} to 10^{-7} of the x-ray energy has been achieved, so far limited only by counting statistics.

3. Calculations

3.1. *Absorption Shift*

On its way from creation to electronic detection the x-ray is exposed to absorption that depends on

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Element	ΔE_a/eV
Tb	-2.0 ± 0.32
Ho	-3.1 ± 0.50
Ta	-3.7 ± 0.60
Re	-3.5 ± 0.57
Os	-3.0 ± 0.50

Table 1. Calculated peak-energy shifts ΔE_a due to K-edge absorption of the K0 x-rays from metallic sources as used in the experiments [15–20].

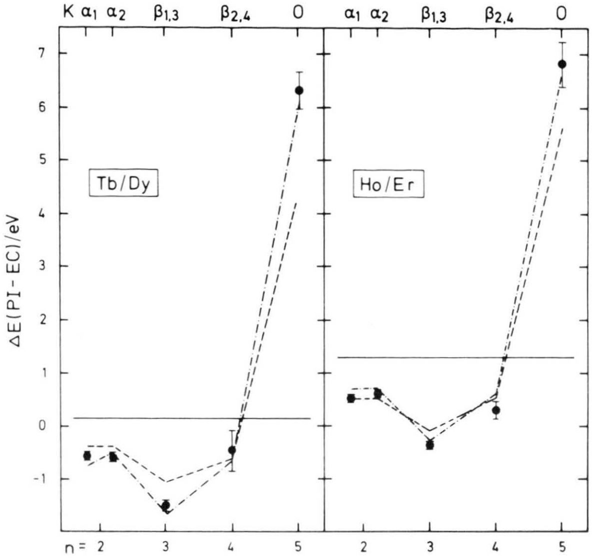

Fig. 1. The energy shifts $E(\mathrm{PI}, n\mathrm{p} \rightarrow 1\mathrm{s}) - E(\mathrm{EC}, n\mathrm{p} \rightarrow 1\mathrm{s})$ ($n=2$ to $n=5$) for K x-rays from metallic samples of rare earth elements. The left hand side shows data for the pair ^{159}Tb(PI)-^{159}Dy(EC)^{159}Tb (18) and the right-hand side shows data for the pair ^{165}Ho(PI)-^{165}Er(EC)^{165}Ho [17]. The experimental results are represented by dots together with the corresponding total uncertainties. The KO-values are corrected for edge absorption. This correction had not been taken into account in the previous data analysis [17, 18]. The horizontal line gives the calculated hyperfine contribution [15, 20]. The dash-dotted lines represent the total theoretical shifts [33] for the assumed configuration "Xe-core" $6s^2\,5d^1\,(4f_{5/2})^6\,(4f_{7/2})^k$, $k=2$, 3, 4 and 5 for terbium, dysprosium, holmium and erbium, respectively. These are the expected configurations for these (trivalent) metals [36]. The dashed lines correspond to the bivalent state in clear discrepancy to the experimental data.

its energy. Because of the finite x-ray line width this leads to a shift of its center of gravity, which is negligible as long as the absorption cross section shows a sufficiently smooth behaviour. On the other hand, a significant influence can be expected when the x-ray energy lies in the immediate vicinity of an absorption edge. This is the case for K0 photons which are excited through photo-fluorescence within the source material [26, 28]; however it will not occur for EC sources. To estimate the corresponding energy shift, the K-edge absorption cross section is approximated by an arctan-function, neglecting the K-edge fine structure [28, 29]. The x-ray line shape is approximated by a Lorentzian. For the geometrical parameters entering the calculations: the source width (typical 0.1 mm), the depth (typical 1 mm), the height (typical 10 mm), the tilting angle (typical 1 °, deduced from the measured line width) and the density, the values of the actual sources of the experiments [15–20] have been used. With realistic estimates concerning the uncertainties of source geometry, line width and cross section [28, 29, 31, 32], the calculations of the peak-energy shifts yield the results given in Table 1.

3.2 Calculation of Transition Energies

The x-ray energies were calculated as difference of the total atomic energies in the initial and final state by means of multi-configuration Dirac Fock programs [33–35] including Breit interaction, vacuum polarization and self-energy. The nuclear charge density is approximated by a two-parameter Fermi-distribution. The calculation starts with a pure ground state configuration to which the 1s or np-hole is coupled in all possible ways. The final x-ray energy is obtained from the weighted mean of these results.

3.3. The Contribution to the Energy Shift

The energy shifts due to the hyperfine effect and the dynamic shift are estimated as given in earlier papers [15–20].

4. Results

4.1. Rare Earth Elements

In the region where the 4f shell is being filled the pairs of sources Tb(PI)-Dy(EC) and Ho(PI)-Er(EC) have been studied. Tb(PI) means that x-rays where excited through photo ionization (PI) of a metallic Tb sample. Dy(EC) means that corresponding x-rays were measured from a radioactive Dy source undergoing electron capture decay (EC). Tb(PI)-Dy(EC) means the energy difference of the equiva-

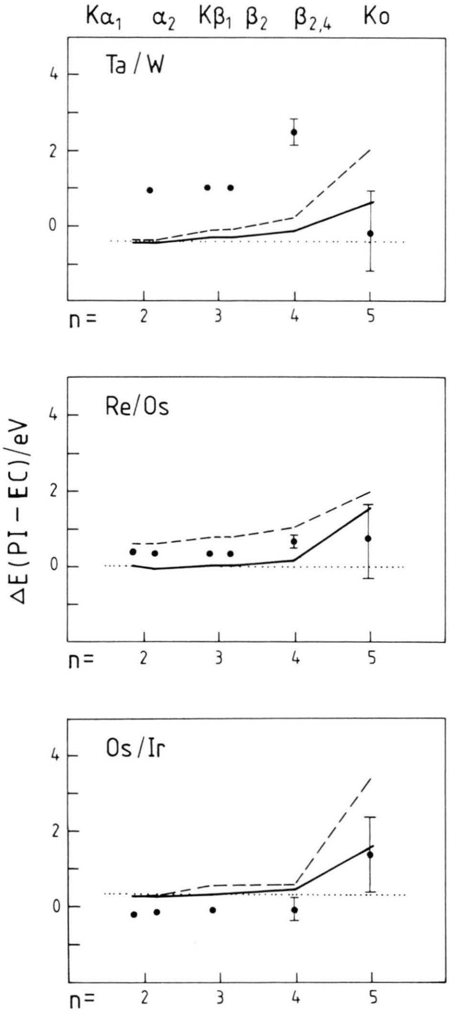

Fig. 2. The energy shifts $E(\mathrm{PI}, n\mathrm{p} \rightarrow 1\mathrm{s}) - E(\mathrm{EC}, n\mathrm{p} \rightarrow 1\mathrm{s})$ in the 5d elements for x-ray transitions as a function of n. The experimental results for three different pairs of elements [18] are given by the dots with corresponding error bars. The dotted lines denote the calculated hyperfine shift. The solid lines correspond to the total shifts for the configurations, with the valence electrons completely bound to the atom, whereas the dashed lines correspond to partially bound valence electrons.

lent x-ray transitions. These elements are especially well suited for a test of the understanding of the atomic structure: they have almost identical chemical properties so that the chemical shift should be absent and the 4f wave functions have a large overlap with inner shells, suggesting a pronounced effect. The results are shown in Fig. 1 together with two different theoretical estimations. The configuration expected for the metallic state of the studied elements is the Xe core, $4\mathrm{f}^{n-1}$, $5\mathrm{d}^1$, $6\mathrm{s}^2$ [36] whereas the free atom configuration should be the Xe core, $4\mathrm{f}^n$, $5\mathrm{d}^0$, $6\mathrm{s}^2$. The energy shifts for these two configurations composed of hyperfine shift, dynamic shift, atomic structure shift and absorption shift are included in the figure. There is quantitative agreement between the experimental data and the calculation assuming a trivalent state, whereas all other configurations can be ruled out.

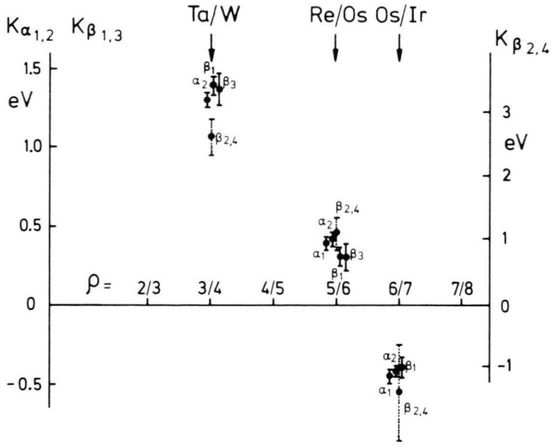

Fig. 3. The differences between experimental and calculated shifts of the Kα and Kβ transitions in the 5d-elements. For each measured pair of elements the differences $\Delta E_{\mathrm{exp}} - \Delta E_{\mathrm{calc}}$ are shown as a function of the 5d occupation umber ϱ. The scales differ for the different transitions. The shift differences from the L, M, N shell seem to follow a linear trend, changing sign at minimum atomic radius.

The situation for the experiment comparing the 4d transition elements $^{103}\mathrm{Rh(PI)}$-$^{103}\mathrm{Pd(EC)}$ remains unchanged, as no absorption shift occurs and the new configuration calculations essentially agree with the old ones [18, 20].

4.2. 5d Transition Elements

In an extensive experiment the following pairs of elements have been studied where the 5d shell is being filled: $^{181}\mathrm{Ta(PI)}$-$^{181}\mathrm{W(EC)}$, $^{185}\mathrm{Re(PI)}$-$^{185}\mathrm{Os(EC)}$ and $^{189}\mathrm{Os(PI)}$-$^{189}\mathrm{Ir(EC)}$ [18–20, 37]. For the strong lines of the first pair there existed already former data from oxide samples that after correction of the chemical shift [11] agree with the new result within the quoted errors [38–40]. The experimental data together with the calculated shifts for two different configurations including hyperfine shift, dynamic shift, atomic structure shift and absorption shift are displayed in Figure 2. The two configurations correspond to the case where the valence electrons are completely or partially itinerant. Besides the values for the K0 transitions there is no large difference between the two models shown in the picture. While the experimental shift pattern is more or less qualitatively reproduced by the calculations, a quantitative discrepancy remains. For the inner K-transitions this discrepancy is shown as function of the 5d shell occupancy in Figure 3. It seems that these shift differences follow a linear trend the origin of which is not yet fully understood. It is interesting to note that this additional energy shift changes sign in a region where the atomic radii and the 5d binding energy have a minimum, so that a solid state effect cannot be excluded [20, 41].

5. Conclusion

In a series of experiments studying the energy of K x-ray transitions with high precision and resolution four effects have been found that shift the energy significantly. These effects originate in the interaction of the atomic electron with the nucleus and with each other, in the different life times of the atomic states and in absorption phenomena in bulk matter. For the rare earth elements these effects seem to be understood quantitatively so that they can be used as probe for studies of nuclear magnetic moments, of atomic structure and atomic relaxation times. For the 5d transition elements an additional effect is observed the origin of which is still an open question.

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