The KLM + KLN Auger electron spectrum of rubidium in different matrices

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Abstract
The KLM + KLN Auger electron spectrum of rubidium (Z = 37) emitted in the electron capture decay of radioactive ⁸³Sr in a polycrystalline platinum matrix and also ⁸⁵Sr in polycrystalline platinum and carbon matrices as well as in an evaporated layer onto a carbon backing were experimentally studied in detail for the first time using a combined electrostatic electron spectrometer. Energies, relative intensities, and natural widths of fifteen basic spectrum components were determined and compared with both theoretical predictions and experimental data for krypton (Z = 36). Relative spectrum line energies obtained from the semi-empirical calculations in intermediate coupling scheme were found to agree within 3σ with the measured values while disagreement with experiment exceeding 3σ was often observed for values obtained from our multiconfiguration Dirac–Hartree–Fock calculations. The absolute energy of the dominant spectrum component given by the semi-empirical approach agrees within 1σ with the measured value. Shifts of + (0.2 ± 0.2) and − (1.9 ± 0.2) eV were measured for the dominant KLM spectrum components between the ⁸³Sr sources prepared by vacuum evaporation on and implanted into the carbon foil, respectively, relative to ⁸⁵Sr implanted into the platinum foil. A value of (713 ± 2) eV was determined for the energy difference of the dominant components of the KLM + KLN Auger electron spectra of rubidium and krypton generated in the polycrystalline platinum matrix. From the detailed analysis of the measured data and available theoretical results, the general conclusion can be drawn that the proper description of the KLM + KLN Auger electron spectrum for Z around 37 should still be based on the intermediate coupling of angular momenta taking into account relativistic effects.

Keywords: ⁸⁵Rb, ⁸⁵Sr, KLM-, KLN- Auger transitions, atomic environment, chemical shift, multiconfiguration Dirac–Hartree–Fock calculations

(Some figures may appear in colour only in the online journal)

1. Introduction

The KLL Auger group is the most intense and the simplest one among the K Auger groups. Consequently, it has been most studied in the past (both theoretically and experimentally). Intensity of other K Auger groups drastically decreases with increasing transition energy while their complexity significantly increases also due to narrowing of the energy intervals they occupy. Thus the total intensity of the KLM Auger group amounts to about 35% of that of the
corresponding KLL one for elements with the atomic number $Z \sim 40$, (see, e.g., [1, 2]) and, according to the intermediate coupling theory [3, 4], its full structure is formed from 36 components (including twelve doublets and three quartets) of very different intensities. Moreover, many close lying components cannot be resolved experimentally due to their natural widths. Thus, the KLM Auger spectrum is actually composed of several overlapping groups of the spectrum lines. Nevertheless, very high instrumental resolution is required even for their separation as well as very thin radioactive sources (several monolayers) to prevent additional line broadening due to inelastic electron scattering in the source material (if the KLM Auger spectra emitted in the radioactive decay are studied). The predicted structure [3, 4] of the KLM Auger spectrum was ‘confirmed’ in several measurements only in the sense that some KLM lines were observed to be broader than expected on the basis of the natural widths of the atomic shells participating in the transitions and/or slightly ‘deformed’.

Intensity of the KLN Auger group in the $Z \sim 40$ region reaches only a few percent of the corresponding KLL group (see, e.g., [2]). Nevertheless, this group complicates experimental investigation of the KLM Auger spectrum due to partial overlapping of these two spectra. The energy interval of the overlap depends on atomic number $Z$ and increases with it.

The complexity of the KLM + KLN Auger spectra and limitations of available electron spectroscopic technique allowed successful experimental research of these spectra mainly in the high $Z$ region in the past. However, radiationless deexcitation of K-shell vacancies dominates in light elements where, moreover, results of the available calculations [2, 3, 5–7] of the KLM transition intensities differ substantially from each other (see also figure 1). The differences are partly caused by various treatment of relativistic effects and/or coupling schemes. Thus the calculations [3, 5] were performed in intermediate-coupling scheme without consideration of relativistic effects while the calculations in jj-coupling were evaluated in both relativistic [2, 7] and non-relativistic [6] approximations. In contrast, the Auger-electron energies are satisfactorily described by, e.g., widely used semi-empirical calculations [4] based on intermediate-coupling and experimental electron subshell binding energies.

So far the KLM Auger spectra of only 12 different elements were measured in detail in the atomic number region $18 < Z < 45$, namely for $Z = 23$ [8–10], 24 [9, 10], 25 [10, 11], 26 [10, 12, 13], 28 [14], 29 [15], 30 [16], 31 [8], 32 [17], 33 [18], 35 [19, 20], and 36 [21].

Experimental data on the atomic environmental effects on the KLM Auger spectra are also scarce especially for medium and heavy elements (i.e., involving core atomic levels). However, such data are of considerable importance for basic research as well as for interpretation of weak structures observed in very complex experimental Auger electron spectra. It was, moreover, found in the experimental investigations (see, e.g., [22, 23]) that energies of the KLM Auger electrons are a quite sensitive probe of changes in local atomic environment. In [22], the krypton KLM Auger spectrum accompanying the electron capture (EC) decay of $^{83}$Rb incorporated in two different solid hosts (a bulk of a high purity polycrystalline Pt foil and a layer evaporated in vacuum on the same type of Pt foil) was studied. The KLM Auger spectrum of rubidium from the EC decay of $^{83}$Sr and $^{85}$Sr atoms situated in three different solid matrices (bulks of a high purity polycrystalline platinum and carbon foils and a layer evaporated in vacuum on the same type of carbon foil) was investigated in [23]. This type of information is also important for some present neutrino experiments. For example, the aim of the neutrino project KATRIN [24] is to measure the mass of electron anti-neutrinos from beta-decay of tritium with an unprecedented sensitivity of 0.2 eV/c$^2$. In order to achieve this upper mass limit, a long-term stability of the energy scale of the main KATRIN electrostatic retardation $\beta$-ray spectrometer at the level of ±3 ppm (i.e., ±60 meV at 18.6 keV) for at least 2 months of continuous measurements is required. In this regard, suitability of the K-32 conversion electrons (kinetic energy of 17.8 keV) of $^{83m}$Kr (generated in the EC decay of $^{83}$Rb) for monitoring of the KATRIN spectrometer energy scale stability was extensively studied in [25, 26]. The results obtained unambiguously indicated that the electron sources prepared by $^{83}$Rb ion implantation into metallic matrices should be preferred. However, the substrate material and implantation conditions are to be optimized. This also requires further extensive experimental investigations of the influence of local physicochemical environments of $^{83}$Rb atoms on the K-32 electron energy. Information on low energy electron spectra emitted in radioactive decay under real condition can also be helpful for another neutrino project, namely ‘EC $^{164}$Ho experiment’ (ECHo) [27, 28] based on high precision and high statistics microcalorimetric measurements of the $^{164}$Ho EC spectrum. An improvement of the theoretical description of this spectrum, in particular by investigating its modification due to the physicochemical

Figure 1. Available experimental data [8–21] (including present value for Rb, the open circle) on the $KL_2M_{3,3}/KL_3M_{3,3}$ transition intensity ratio are displayed as a function of the atomic number $Z$. Theoretical predictions are also depicted: nonrelativistic calculations in intermediate coupling [3]—NR, IC-1, [5]—NR, IC-2; nonrelativistic calculations in jj-coupling [6]—NR, jj; relativistic calculations in jj-coupling [2]—R, jj.
nuclide of rubidium following the EC decay of the $^{83}\text{Sr}$ isotope. The study was performed within the development of super-stable calibration $^{83}\text{Rb}^{/83m}\text{Kr}$ electron sources for the above-mentioned international project KATRIN. It should be noted that the KLM $+$ KLN Auger spectrum of rubidium ($Z = 37$) was measured in this work for the first time.

2. Experimental

2.1. Source preparation

2.1.1. Ion implantation. The $^{83}\text{Sr}$ and $^{85}\text{Sr}$ radionuclides were produced by spallation of metallic yttrium by 300 MeV protons from the internal beam of the synchrocyclotron particle accelerator at the JINR, Dubna. A chemical treatment of the irradiated target as well as the preparation of the implanted $^{83}\text{Sr}$ and $^{85}\text{Sr}$ sources are described in detail in [23].

Using the computer code SRIM [34], we performed a Monte-Carlo simulation of the $^{83}\text{Sr}$ and $^{85}\text{Sr}$ ion implantations with the aim to obtain some information on the ion depth distributions. Real circumstances of our implantations were taken into account, namely the zero ion incident angle (relative to the source foil normal), polycrystalline structure of the platinum and carbon foils as well as an adsorbed surface contamination layer represented by an additional 3 nm thick pure carbon layer on the foil surfaces [35]. Results of the simulations (representing, in fact, depth probability distributions) are displayed in figure 4. As can be seen from the figure, the $^{85}\text{Sr}$ ions were embedded deep below the surface in the case of the carbon foil. The average ion range reaches 21.4 nm (including the 3 nm thick contamination layer). In contrast, the average $^{83}\text{Sr}$ and $^{85}\text{Sr}$ ion ranges in the platinum foils were calculated to be respectively only 9.1 and 9.0 nm. Moreover, portions of about 7% and 10% of the incident $^{83}\text{Sr}$ and $^{85}\text{Sr}$ ions, respectively, were found in the surface contamination layers which exhibit different physicochemical properties than the corresponding bulk foil material. The above number was experimentally proved in the case of the implantation of $^{83}\text{Rb}$ into the similar Pt foil [25, 26].

It should be noted that the prepared sources were exposed to air during their transfer to the electron spectrometer. As a result, the $^{83}\text{Sr}$ and $^{85}\text{Sr}$ ions in the contamination layers were bound with oxygen in all possible forms (oxides, hydroxides, carbonates, hydrocarbonates, etc) characterized by the oxidation number $+2$ (as in the case of the $^{85}\text{Sr}$ source produced by evaporation in vacuum, see below the section 2.1.2.). These contamination layers, however, were not taken away before the electron spectrum measurements.

2.1.2. Thermal vacuum evaporation deposition. Several drops of the strontium fraction were dried up in a Ta environment of $^{163}\text{Ho}$ atoms is required to search for the electron neutrino mass in the energy range below 1 eV.

Auger-electron emitting radioisotopes have always been an interest to the nuclear medicine society [29]. Cellular dosimetry of these radioisotopes largely depends on their energy spectra. However, experimental spectra of these radioisotopes are scarce, even for the K Auger electrons, and thus most dosimetry workers rely on theoretical energy spectra. However, experimental spectra of these radioisotopes are scarce, even for the K Auger electrons, and thus most dosimetry workers rely on theoretical energy spectra based on computer models that simulate the atomic relaxation [30, 31]. New measurements are needed for benchmarking of these models in order to minimize the uncertainty of dosimetry calculation.

In this paper we present results of our detailed experimental study of the KLM $+$ KLN Auger electron spectrum of rubidium following the EC decay of the $^{83}\text{Sr}$ ($T_{1/2} = 32.4$ h) and $^{85}\text{Sr}$ ($T_{1/2} = 64.9$ d) atoms (see figures 2, 3) embedded into different host matrices. Sources of $^{85}\text{Sr}$ were produced by evaporation in vacuum on a polycrystalline carbon backing ($C_{\text{evap}}$) and by ion implantation at 30 keV into both high purity polycrystalline platinum ($\text{Pt}_{\text{impl}}$) and carbon ($C_{\text{impl}}$) foils as well. Ion implantation at 30 keV into the same Pt foil was employed for preparation of the $^{83}\text{Sr}$ source.

Figure 2. The incomplete decay schemes of the $^{83}\text{Sr}$ radioisotope [32].

Figure 3. The incomplete decay schemes of the $^{85}\text{Sr}$ isotope [33].
implanted at 30 keV into the high purity polycrystalline platinum
parent 85Sr matrices. The exact chemical state of 85Sr in the deposited layers in
vacuum after the preparation was unknown. However, the 85Sr
sources were transferred to the electron spectrometer in air.

Thus due to the extreme strontium reactivity, the 85Sr ions
created with oxygen all possible forms (oxides, hydroxides, 
carbonates, hydrocarbontes, etc) and exhibited the +2
oxidation state. The most of the parent 85Sr atoms were
apparently in the chemical form SrCO3. The daughter 85Rb ions
(generated in the 85Sr EC decay) were then stabilized in the
mentioned 85Sr matrices. Consequently, the 85Rb ions

probably formed with oxygen anions all possible relevant forms (O2−, OH−, CO32−, HCO3−, etc). But contrary to 85Sr, they had the oxidation number +1. Similar experiments from
the past (performed, e.g., with 99mTc [36–38]) support these
conclusions.

2.2. Measurements and energy calibration

The electron spectra were measured by means of a combined
electrostatic electron spectrometer [39] consisting of a
retarding sphere (an integral spectrometer) followed by a
double-pass cylindrical mirror energy analyzer (CMEA) (a
differential spectrometer), a schematic view of the spectrometer
shown in figure 5. The two-stage construction of the
CMEA analyzer is employed for suppression of the spectro-

trometer background caused by scattered and non-axial elec-
trons. There are several measuring modes. In the basic mode,
the retarding sphere (2) is grounded and the scanning
retarding positive potential is applied to the investigated
electron source (1). The slowed-down electrons enter the
CMEA through the annular conic slit (3) where their energies
are analyzed by the constant negative voltage applied to the
outer coaxial cylinder (5). The inner cylinder (4) is grounded.
The analyzed electron beam is delimited by four circular slits
(3, 6) on the inner cylinder. The electron detector (a window-
less channel electron multiplier, CEM) is situated in the
second focus (F2). Because the electrons have the same
kinetic energy given by the above mentioned negative analy-
zing voltage, they are detected at the same CEM detection
site (5). In order to improve homogeneity of the evaporated
layer, the source backing with the mask rotated around their common axis at a speed of 3000

turns min−1 at a distance of about 8 mm from the evaporation
boat. No visible effects were found on the backing surfaces
after the evaporation. Altogether two 85Sr sources with
activities of 2.3 and 1.1 MBq (just after the evaporation) were
prepared.

It should be noted that the amount of the 85Sr atoms in each
of the prepared sources reached only several nanograms.
Therefore, the use of general chemistry terms in this case is
questionable. Keeping this in mind, the chemical state of the
85Rb atoms can be characterized as impurity state in the
parent 85Sr matrices.

The exact chemical state of 85Sr in the deposited layers in
vacuum after the preparation was unknown. However, the 85Sr
evaporation at 1400 °C lasted several seconds. A mask with a
circular opening of 8 mm diameter was used to define the
source area on the backing. In order to improve homogeneity
of the evaporated layer, the source backing with the mask
rotated around their common axis at a speed of 3000

turns min−1 at a distance of about 8 mm from the evaporation
boat. No visible effects were found on the backing surfaces
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The exact chemical state of 85Sr in the deposited layers in
evacuum after the preparation was unknown. However, the 85Sr
A value of less than 0.1 eV was estimated for the recoil kinetic energy $E_{\text{rec}}(i)$ of an atom after the emission of any of our calibration conversion electrons. For the energy calibration, sources of the parent $^{169}\text{Yb}$ and $^{57}\text{Co}$ isotopes prepared by vacuum evaporation on polycrystalline carbon backing were used. This should provide that local surrounding of the daughter $^{169}\text{Tm}$ and $^{57}\text{Fe}$ atoms and those used for the determination of the Tm and Fe electron binding energies are very close to each other. Nevertheless, we examined the influence of the maximum measured chemical shifts of binding energies of about 2 and 4 eV [45] for the Tm and Fe valence electrons on the energy calibration. It was found to be well below the standard deviations of the measured absolute electron energies quoted in table 1 and in the text.

A relation between the above mentioned electron retarding positive voltage $U_r$ (in V) applied to the radioactive source and the negative analyzing voltage $u_a$ (in V) applied to the outer coaxial cylinder of the CMEA from one side and the kinetic energy $E_e$ (in eV) of the detected electrons from other side can be expressed by the following equation in the investigated energy range:

$$E_e = 1.000 \pm 0.004 \cdot 44(5) \cdot [U_r + 1.833(2)(u_a - 100)] + 189.4(5),$$

where $1.000 \pm 0.004$, 1.833(2), and 189.4(5) mean $1.000 \pm 0.00005$, 1.833 ± 0.002, and 189.4 ± 0.5, respectively.
Figure 8. An overview of the low-energy electron spectrum accompanying the EC decay chain of $^{83}$Sr (see figure 2) as measured by the combined electrostatic electron spectrometer [39], i.e., without any correction for both the spectrometer transmission drop and the daughter $^{83}$Rb isotope, with 7 eV instrumental resolution and 30 s exposure per spectrum point. Electrons emitted in the EC decay of the daughter $^{83}$Rb isotope are also well seen in the spectrum. A spectrum region containing the KLM Auger electron spectrum of Kr (partly) and Rb (full) is displayed on an enlarged scale in the insert.

2.3. Spectra evaluation

To decompose the measured spectra into individual components, the method described in [46] was employed. This approach, the single spectrum line shape is expressed as the convolution of a Gaussian (representing the spectrometer response function to monoenergetic electrons) and an artificially created function based on a Lorentzian (the natural energy distribution of the investigated electrons leaving atoms). A description of the contributing energy loss spectra (exhibiting rather complicated structure) with sufficient accuracy is a very difficult task though some progress is being made in this field (see, e.g., [35, 47–50]). To solve this problem, we applied the Monte Carlo approach in the spectra evaluation. It is based on manifold fitting of the experimental spectrum with random variations of the single line shape in its energy loss region within the pre-set shape limits. The starting approximations were obtained from suitable components of the evaluated spectrum. More details on the approach used can be found, e.g., in [23]. The position, the height, and the width of each fitted spectrum line, the constant background and the width of the spectrometer response function were the fitted parameters. The results obtained are shown in figures 1, 6 and 7 by continuous lines, in tables 1–3 and in the text. The quoted uncertainties are our estimates of standard deviations ($\sigma$).

3. Calculations

Wave functions describing initial and final ion states of the Auger electron transitions are calculated using the relativistic atomic structure package GRASP2K [51], relying on the multiconfiguration Dirac–Hartree–Fock (MCDHF) approach and jj-coupling scheme. A natural starting point in fully relativistic calculations is the Dirac–Coulomb Hamiltonian, which is given by

$$H_{DC} = \sum_{i=1}^{N} \left[ c_\alpha p_i + (\beta_i - 1) e^2 + V_N(r_i) \right] + \sum_{i<j}^{N} \frac{1}{r_{ij}}. \quad (3)$$

where $V_N(r)$ is the monopole part of the electron–nucleus interaction, $r_{ij}$ is the distance between electrons $i$ and $j$, and $\alpha$ and $\beta$ are the Dirac matrices. In MCDHF theory, approximate eigen functions to the Dirac–Coulomb Hamiltonian above are the so-called atomic state functions (ASFs), $\Psi(\gamma|JM)$, which are expansions over configuration state functions (CSFs), $\varphi(\gamma|JM)$, with total angular momentum $J$ symmetry and parity $P$:

$$\Psi(\gamma|JM) = \sum_{i=1}^{N_{CSF}} c_i \varphi(\gamma|JM). \quad (4)$$

In the expression above, $\gamma$ represents the configuration, coupling and other quantum numbers necessary to uniquely describe the state, $M$ is the projection of $J$ on the $z$-axis and $c_i$ is the expansion coefficient. Since electron correlation is not taken into account in the present work, the calculations are performed using the Dirac–Hartree–Fock (DHF) approach. However, since the CSFs in GRASP2K are generated using non-relativistic configurations as input, an ASF may also in this case be expanded over several interacting CSFs, representing different relativistic configurations and couplings. The advantage of this approach is that intermediate coupling is taken into account and thus a good description of the resulting ASFs is provided also when mixing of jj-coupled states is expected to be significant [52]. The CSFs are constructed from the one-electron Dirac orbitals, where the radial wave functions together with the expansion coefficients are obtained in a relativistic self-consistent-field procedure [53]. The transverse photon interaction as well as the leading quantum electrodynamic corrections are accounted for in subsequent relativistic configuration interaction calculations [54].

Once a set of ASFs are obtained, the Auger transition amplitude for the autoionization of the inner-shell excited initial state $|\Psi(\gamma|P|JM)\rangle$ into the final scattering state $|\Psi(\gamma|P|JM)\rangle$ is computed using RATIP [55] according to [56]:

$$V_{L,M} = \langle \Psi(\gamma|P|JM) \rangle \langle \Psi(\gamma|P|JM) \rangle e_{ss} \delta_{MM} \delta_{PP} \delta_{PP}. \quad (5)$$

In the expression above, $V$ denote the sum of the Coulomb electron–electron interaction and the Breit interaction. The possible final scattering states are obtained by coupling each possible state of the final ion $|\Psi(\gamma|P|JM)\rangle$ to the wave function of the corresponding outgoing electron with relativistic angular momentum $\omega$. The energy of the outgoing electron is given by the energy difference of the initial and final ion states and the continuum wave function of the outgoing electron is generated within the optimized level potential of the final state and kept orthogonal to the final

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The measured energies (in eV) of the KLM + KLN Auger transitions in $^{85}$Rb (relative to the energy of the KL$_3$M$_2$(3P$_0$, 3S$_1$) + KL$_3$M$_3$(3P$_0$) line group) following the electron capture decay of $^{85}$Sr evaporated on a polycrystalline carbon foil ($C_{\text{evap}}$). The data are compared with results from both the semi-empirical calculations [4] and those performed in the present work (see section 3).

Table 1. The measured energies (in eV) of the KLM + KLN Auger transitions in $^{85}$Rb (relative to the energy of the KL$_3$M$_2$(3P$_0$, 3S$_1$) + KL$_3$M$_3$(3P$_0$) line group) following the electron capture decay of $^{85}$Sr evaporated on a polycrystalline carbon foil ($C_{\text{evap}}$). The data are compared with results from both the semi-empirical calculations [4] and those performed in the present work (see section 3).

| Line No | Transition(s)$^b$ | Transition(s)$^b$ | Experiment This work | Reference [4]$^d$ | DL | Reference [4]$^d$ | This work$^e$ | DTW |
|---------|------------------|------------------|----------------------|------------------|-----|------------------|----------------|-----|
| 1       | KL$_1$M$_1$(1S$_0$, 3S$_1$) | KL$_1$M$_1$(1S$_0$, 3S$_1$) | -340.8(7)$^f$ | -339.0 | -1.8(7) | -339.0 | -344.7 | +3.9(7) |
| 2       | KL$_1$M$_2$(3P$_0$, 3P$_1$) | KL$_1$M$_2$(3P$_0$, 3P$_1$) | -260.5(8) | -259.4 | -1.1(8) | -259.4 | -265.5 | +5.0(8) |
| 3       | KL$_1$M$_3$(3P$_0$, 3P$_2$) | KL$_1$M$_3$(3P$_0$, 3P$_2$) | -250.9(9) | -251.0 | +0.1(9) | -250.6 | -256.0 | +5.1(9) |
| 4       | KL$_2$M$_1$(3P$_0$, 3P$_1$) + KL$_2$M$_3$(3P$_0$, 3P$_2$) | KL$_2$M$_1$(3P$_0$, 3P$_1$) + KL$_2$M$_3$(3P$_0$, 3P$_2$) | -132.2(9) | -133.9 | +1.7(9) | -132.9 | -131.9 | -0.3(9) |
| 5       | KL$_2$M$_1$(3P$_0$, 3P$_1$) | KL$_2$M$_1$(3P$_0$, 3P$_1$) | -76.7(12) | -75.5 | -1.2(12) | -73.0 | -73.1 | -3.6(12) |
| 6       | KL$_2$M$_2$(1S$_0$) | KL$_2$M$_2$(1S$_0$) | -68.6(12) | -65.6 | -3.0(12) | -65.6 | -66.8 | -1.8(12) |
| 7       | KL$_2$M$_3$(3P$_2$, 3P$_1$) + KL$_2$M$_3$(3P$_1$) | KL$_2$M$_3$(3P$_2$, 3P$_1$) + KL$_2$M$_3$(3P$_1$) | -50.7(3) | -51.2 | +0.5(3) | -51.2 | -50.8 | 0.1(3) |
| 8       | KL$_1$N | KL$_1$N | -23.1(10) | -17.3 | -5.8(10) |
| 9       | KL$_3$M$_2$(3P$_0$, 3P$_1$) + KL$_3$M$_3$(3P$_0$, 3P$_1$) | KL$_3$M$_2$(3P$_0$, 3P$_1$) + KL$_3$M$_3$(3P$_0$, 3P$_1$) | 13 121.9(13)$^g$ | 13 120.6$^g$ | -1.3(13) | 13 120.6$^g$ | 13 107.1$^h$ | -14.8(13) |
| 10      | KL$_3$M$_2$(3P$_2$, 3P$_3$, 3P$_1$) | KL$_3$M$_2$(3P$_2$, 3P$_3$, 3P$_1$) | +6.1(5) | +5.9 | -0.2(5) | +6.2 | +6.7 | +0.6(5) |
| 11      | KL$_3$M$_2$(3P$_0$, 3P$_1$) | KL$_3$M$_2$(3P$_0$, 3P$_1$) | +78.5(8) | +81.9 | +3.4(8) |
| 12      | KL$_3$M$_2$(3P$_0$, 3P$_1$) | KL$_3$M$_2$(3P$_0$, 3P$_1$) | +136.1(8) | +140.4 | +4.3(8) |
| 13      | KL$_2$N$_{2,3}$ | KL$_2$N$_{2,3}$ | +195.8(11) | +194.3 | -3.3(11) |
| 14      | KL$_1$N$_1$ | KL$_1$N$_1$ | +236.3(13) | +236.5 | +0.2(13) |
| 15      | KL$_3$N$_{2,3}$ | KL$_3$N$_{2,3}$ | +253.9(8) | +258.7 | +4.8(8) |

DL—Differences between the values obtained from the semi-empirical calculations [4] for the dominant components and the experimental data.

DTW—Differences between the values obtained from the present calculations for the dominant components and the experimental data.

$^a$ Transitions labeled by GRASP2K module JJ2LSJ.

$^b$ Energies of the dominant component of the individual line group related to the energy of the KL$_3$M$_2$(3P$_2$, 3S$_1$) component.

$^c$ Differences of the line group energies determined as weighted means of the semi-empirical transition energies [4] and the theoretical transition intensities [3] of the corresponding line group components.

$^d$ Calculations performed for the Auger transitions in $^{85}$Rb following the electron capture decay of $^{85}$Sr.

$^e$ The absolute energy related to the Fermi level.

$^f$ The absolute energy related to the vacuum level.

$^g$ The absolute energy related to $^{85}$Sr.
Table 2. The measured relative intensities (in %) of the KLM + KLN Auger transitions in $^{85}\text{Rb}$ following the electron capture decay of $^{85}\text{Sr}$ evaporated on a polycrystalline carbon foil (Cevap) compared with results of the calculations [2, 5] and those performed in the present work.

| Line No | Transition(s) | Experiment | Theory $^a$ |
|---------|---------------|------------|-------------|
|         |               | This work $^b$ | This work $^c$ | Reference [21] $^c$ (Kr) | Reference [2] $^d$ | Reference [5] | This work |
| 1       | KL$_1$M$_1$($^3$S$_0$, $^1$S$_1$)$^e$ | 8.3(5)$^f$ | 10.0(6) | 9.8(3) | 9.9 | 8.2 | 10.9 |
| 2       | KL$_1$M$_2$($^3$P$_1$, $^1$P$_0$) | 7.9(8) | 9.5(9) | 17.0(13) | 7.8(4) | 17.1(6) | 5.6 | 6.4 | 7.5 |
| 3       | KL$_1$M$_3$($^3$P$_1$, $^1$P$_2$) | 6.2(8) | 7.5(9) | 9.3(4) | 9.2 | 7.6 | 8.8 |
| 4       | KL$_2$M$_1$($^3$P$_1$, $^1$P$_0$) + KL$_1$M$_4.5$ | 3.6(5) | 4.3(6) | 5.6(4) | 5.7 | 4.4 | 6.3 |
| 5       | KL$_3$M$_1$($^3$P$_1$, $^1$P$_2$) | 4.4(8) | 5.3(9) | 9.5(13) | 5.9(2) | 8.4(3) | 8.5 | 7.7 | 7.9 |
| 6       | KL$_2$M$_3$($^3$S$_0$) | 3.5(8) | 4.2(9) | 2.5(2) | 1.7 | 2.4 | 2.3 |
| 7       | KL$_3$M$_3$($^3$D$_2$, $^3$D$_1$) + KL$_2$M$_3$($^3$P$_1$) | 20.2(11) | 24.3(15) | 24.9(6) | 18.2 | 25.9 | 23.16 |
| 8       | KL$_1$N | 2.4(4) | 2.9(5) | 1.4(2) | 3.0 |
| 9       | KL$_3$M$_3$($^3$P$_2$, $^3$S$_1$) + KL$_1$M$_4$($^3$P$_0$) | 23.7(15) | 28.5(19) | 36.6(24) | 28.8(12) | 35.5(13) | 20.2 | 25.2 | 24.6 |
| 10      | KL$_2$M$_4$($^3$D$_2$, $^3$D$_3$, $^1$P$_1$) | 6.7(12) | 8.1(14) | 6.7(6) | 22.1 | 12.3 | 9.3 |
| 11      | KL$_3$M$_4$ | 2.6(3) | 3.1(4) | 3.3(2) | 2.6 | 3.1 |
| 12      | KL$_2$M$_4$ | 3.6(3) | 4.3(4) | 4.7(3) | 6.0 | 4.8 |
| 13      | KL$_2$N$_{2,3}$ | 2.5(3) | 3.0(4) | 2.1(1) | 2.6 |
| 14      | KL$_3$N$_1$ | 0.7(2) | 0.8(2) | 0.6(1) | 1.0 |
| 15      | KL$_3$N$_{2,3}$ | 3.7(3) | 4.5(4) | 4.1(2) | 3.8 |
| 10/9    | KL$_1$M$_1$/$^1$KL$_1$M$_2$ $^b$ | 0.28(5) | 0.23(2) | 0.23(2) | 1.09 | 0.49 | 0.38 |
|         | KL$_2$M$_3$/$^3$KL$_2$M$_3$ | 1.30(5)$^f$ | 1.30(3) | 2.13 | 1.32 | 1.31 |

$^a$ Lines or line groups identified by means of the semi-empirical Auger transition energies [4].
$^b$ Normalized to $\Sigma$(KLM + KLN).
$^c$ Normalized to $\Sigma$KL$_{1-3}$M$_{1-3}$.
$^d$ For $Z = 36$ (Kr).
$^e$ The dominant component of the multiplet is highlighted by bold.
$^f$ 8.3(5) means $8.3 \pm 0.5$.
$^g$ Normalized to $\Sigma$KLN.
$^h$ See section 4.3 for explanation.
$^i$ The weighted mean of the values obtained also from the measurements with the Cimpl and Ptimpl sources (see figure 7).
state orbitals. Finally, the Auger transition probability is given by

\[
A_{i,j,l} = \frac{2\pi (V_{i,j,l})^2}{\hbar}.
\]  

(6)

In RATIP, the so-called frozen core approximation must be used, and thus a common orthonormal basis with one-electron Dirac orbitals describing the initial state is used for the computation of the Auger transition probability. The validity of this approximation for strong KLL transitions in krypton (Z = 36) has been studied in [57]. In this work it was found that transitions rates in the frozen core approximation are approximately 20% larger than transition rates obtained using fully relaxed wave functions. An estimate of the relaxation effect can also be obtained by comparing transition rates in the frozen core approximation using initial state wave functions and final state wave functions, respectively. Such an analysis results in a maximum discrepancy of 12% for stronger transitions (A > 10^{13} s^{-1}). Since transition rates are consistently overestimated in the frozen core approximation, the error in the computed relative intensities in the last column of table 2 due to relaxation effects are expected to be smaller and estimated to be around 10%. The energy of the outgoing Auger electron, however, is obtained as the energy difference of the initial state and the final ion state using one-electron on the 5s shell

\[
\text{Table 3. Natural widths (in eV) of some fitted spectrum components of the KLM + KLN Auger electron spectrum of } ^{85}\text{Rb emitted in the electron capture decay of } ^{85}\text{Sr evaporated on a polycrystalline carbon foil.}
\]

| Line | Spectrum component | This work | Estimated\* |
|------|-------------------|-----------|-------------|
| 1    | KL1M1             | 11.6(18)  | 10.7(11)    |
| 2    | KL1M2             | 8.5(25)   | 8.6(10)     |
| 3    | KL1M3             | 7.5(25)   | 8.7(10)     |
| 4    | KL2M1(3P3/2, 3P1/2 + KL1M4,5) | 9(3) | 8.3(6) |
| 5    | KL3M1(3D3/2, 3D1/2 + KL2M1 + KL1M5) | 5.3(7) | 6.3(5) |
| 6    | KL2M5(P3/2) + KL1M4(1P1) | 4.9(13) | 6.1(5) |
| 7    | KL3M5(P3/2, 3P1) + KL2M5(P3/2) | 5.9(13) | 6.2(5) |
| 8    | KL2M5,5           | 5.6(19)   | 4.4(5)      |
| 9    | KL2N2,3           | 8.5(25)   |             |
| 10   | KL2N2,3           | 3.3(11)   |             |

* A sum of natural widths of the atomic levels participating in the Auger transition.
\* 11.6(18) means 11.6 ± 1.8.
\* A value evaluated for the KL1M1 transition.
\* A value evaluated for the KL2M1 transition.
\* A value evaluated for the KL1M5 transition.
\* A value evaluated for the KL2M1 transition.

atomic configuration of a neutral rubidium system (i.e. only one electron on the 5s shell) was assumed in the calculations, while an extra 5s electron was included for the EC decay, corresponding to the 5s^2 valence-shell configuration of a neutral Sr atom. The results obtained are presented in tables 1 and 2 and in the text.

3.1. Labeling of Auger transitions

Following accepted convention (see, e.g., [4]), KXY Auger transitions are in the present work uniquely labeled using a combination of jj-coupling of electron–holes in the initial and final states and LSJ-coupling of the final state. For example, a transition in Rb between an initial state with a hole in the 1s subshell (K) and a final state with holes in the 2p3/2 (L3) and 3s (M1) subshells which couples to ^3P in 2s+1L3 notation will be labeled KL1M1 ^3P. The problem with this notation is that jj-coupling is only expected to be valid in the high-Z limit where the spin–orbit interaction is strong, whereas pure LSJ-coupling is present only in the low-Z limit. To facilitate comparison with other works, we use in what follows the notation by Larkins [4] obtained in the high/low Z limits discussed above, although this is not correct in all cases for rubidium. For comparison, in the second column of table 1, we give the notation optimized for rubidium as given by the JJ2LSJ module of the GRASP2K package, which provides a reliable conversion between the jj- and LSJ-coupling schemes [58]. Indeed, as seen in table 1, the two sets of notations differ for several transitions emphasizing that the conventional labeling of Auger transitions is far from trivial.

4. Results and discussion

As can be seen from figure 6, we were able to reasonably fit only 15 components to the measured KLM + KLN Auger spectrum. Their identification was performed on the basis of the widely used semi-empirical Auger-electron energies [4]. In some cases, however, reliability of the results obtained was greatly reduced due to a strong correlation of the fitted parameters. This concerns, in particular, complex multi-component groups like KL1M2,3 and KL2M1 + KL2M2,3.

It is seen from figure 7 that the measured dominant KL2M2,3 line groups exhibit very similar structure for the ^85Sr sources prepared by ion implantation in Pt and C substrates despite significantly different substrate atomic numbers Z and ion implantation profiles (see figure 4). On the other hand, the discrete energy loss peaks of the spectrum components are much higher for the ^85Sr source prepared by vacuum evaporation deposition on the carbon foil than for the above implanted sources. This difference can only be explained by a greater effective thickness for the inelastic electron scattering in the case of the evaporated ^85Sr source.
4.1. Transition energies

In the evaluation, the absolute energy (related to the Fermi level) of the dominant and well separated KL2M2(3P2, 3S1) + KL3M3(3P0) spectral component (line No. 9) as well as energies of other spectral components relative to this one were determined. They are given in Table 1 together with results of both the semi-empirical energy calculations [4] for rubidium (4th–6th columns) and the ab initio calculations performed in the present work for our specific case, i.e., for the KLM + KLN Auger transitions in 85Rb following the EC decay of 85Sr (7th and 8th columns). In the case of the semi-empirical calculations [4], the relative energies are given as for the dominant components of the fitted line groups (4th column) as for the fitted line group energies determined as weighted mean of the semi-empirical transition energies [4] of the corresponding line group components using the theoretical transition intensities [3] (6th column).

It is seen from Table 1 that the relative semi-empirical energies [4] agree with the measured values within 3σ (see 5th column) while disagreement with experiment exceeding 3σ is often observed for values obtained from our ab initio calculations (see the last column). Moreover, the energy interval occupied by the KLM spectrum (i.e. from the first to the last spectrum lines) calculated in the present work is wider by (8.2 ± 1.1) eV than the experimental one (485.1 eV contrary to (476.9 ± 1.1) eV). The calculated energies in this work are found to be lower than the semi-empirical or observed ones by about 15 eV. This can be mainly attributed to the vapor–metal shifts of Auger-electron energies [59, 60], as the theoretical energies calculated in this work are referenced to the vacuum level, whereas the semi-empirical and observed energies are referenced to the Fermi level. The lack of treatment for the electron correlation effects (as mentioned in section 3) in the calculation could also contribute to these discrepancies at a smaller magnitude [61]. It should be, however, noted that the value of 9.5 eV obtained from our calculations for the separation of the KL2M2 and KL3M3 spectrum lines (i.e. the spectrum components Nos. 2 and 3) closely matches the experimental one (9.6 ± 0.6) eV. Values of 8.4 eV (determined from the dominant transition energies) and 8.8 eV (determined from the weighted mean energies of these two components) were obtained from the semi-empirical calculations [4]. In the case of the separation of the KL2M2(3P2, 3S1) + KL3M3(3P0) and KL2M2(3D2, 3D1, 3P1) components (fitted lines Nos. 9 and 10), the both semi-empirical energies [4] 5.9 eV (dominant transition energies) and 6.2 eV (weighted mean energies) as well as our theoretical value of 6.7 eV matched well with the experimental value of (6.1 ± 0.5) eV. As can be seen from Table 1, the same situation is observed for the separation of the most intense spectrum components KL2M2(3D2, 3D1) + KL3M3(3P1) and KL2M2(3P2, 3S1) + KL3M3(3P0) (fitted lines Nos. 7 and 9).

As can be seen from Table 1, the absolute energy (related to the Fermi level) of the dominant fitted component (No. 9) determined as the weighted mean of the semi-empirical energies [4] and the theoretical intensities [3] of the KL2M2(3P2, 3S1) + KL3M3(3P0) Auger transitions (the 6th column) is identical with the absolute energy of the KL2M2(3P2) Auger transition as the rates [3] for the KL2M2(3P0) and KL3M3(3S1) transitions reach only 15 and <1 per cent, respectively, of the KL2M2(3P2) term. This value agrees very well (within 1σ) with the measured absolute energy (also related to the Fermi level) of the fitted component No. 9. Contrary, our calculated value for the KL2M2(3P2) transition is lower by (14.8 ± 1.3) eV though it is related to the vacuum level. If the work function of 2.6 eV [62] for the polycrystalline strontium (the probable matrix of the daughter rubidium atoms) is taken into account, then the discrepancy found is enlarged up to (17.4 ± 1.3) eV. There are, however, sound reasons to suppose that the work function of our spectrometer should be taken into account, i.e. that one of aluminum oxide which amounts to about 4 eV.) But application of the correction [4] of the Auger transition energies for the solid-state effect using the value of 6.0 eV [4] for the solid-state correction term of strontium increases our calculated energy of the KL2M3(3P2) transition to 13110.8 eV, i.e. the above discrepancy is reduced to (11.4 ± 1.3) eV. Further increase of our calculated KLM + KLN Auger transition energies in rubidium (resulting in improvement of the agreement between our energy calculations and experimental values) is expected when experimental electron binding energies rather than the ab initio binding energies (which was adopted in our calculations) are used.

Quite different situation was discovered [23] in the case of the KLL Auger spectrum of rubidium measured with the same evaporated source on the polycrystalline carbon foil. The measured absolute energy (related to the Fermi level) of the dominant KLL(1D2) transition was found to be higher by (6.1 ± 1.6) eV than the semi-empirical prediction [4]. On the basis of various facts, the authors [23] came to a conclusion that the observed growth of the experimental KLL transition energy was mainly caused by so-called ‘atomic structure effect’ (see, e.g., [63]) that was revealed for the first time in the holmium K x-rays. The lifetime of the 1s atomic holes arising in the EC decay is so short (10−16–10−17 s) that the outer-electron configuration of the intermediate atomic state is very close to that of the parent atom. Due to additional screening of the daughter nucleus by a ‘spectator’ electron, energies of the K Auger transitions induced by the EC decay increase through a decrease of the relevant electron binding energies. The effect was found to be the most pronounced in x-rays for the 4f and 5f rare earth elements.

In the case of rubidium (belonging to the ‘5s elements’), the influence of the ‘atomic structure effect’ is expected to be less pronounced for the K Auger transition energies. According to our calculations, the absolute energies of the KLM + KLN Auger transitions following the creation of initial vacancies by the IC processes in the 85Sr daughter decays are lower by (6.9 ± 0.1) eV than those induced by the EC decay of 85Sr. The uncertainty in the shift is the standard deviation of the differences in peak positions in folded line spectra. The folding procedure ensure that the number of dominant components is the same in the two spectra, although the number of unfolded lines differ substantially. However, the different reference level used in our calculations and the
different phase of matter considered did not enable us to investigate the influence of the 'atomic structure effect' on the KLM + KLN Auger spectrum emitted in the $^8{\text{Sr}}$ decay.

As mentioned above (see section 2.1), three different $^8{\text{Sr}}$ sources (namely C$_{\text{evap}}$, P$_{\text{impl}}$, and C$_{\text{impl}}$) were prepared in order to investigate the influence of the physicochemical environment of the daughter $^8{\text{Rb}}$ atoms on the KLM spectrum of Auger electrons emitted in their deexcitation. The dominant line groups of the spectra measured with these sources are compared in figure 7. It is seen from the figure that the positions of the two most intense components KL$_2$M$_2$(3D$_2$, 3D$_1$) + KL$_2$M$_2$(P$_1$) (No. 7) and KL$_3$M$_3$(P$_2$, $^3$S$_1$) + KL$_3$M$_3$(P$_0$) (No. 9) are almost the same for the C$_{\text{evap}}$ and P$_{\text{impl}}$ while those for the C$_{\text{impl}}$ are slightly lower. From the energies of these two lines as well as the KL$_3$M$_3$(D$_2$, D$_3$, P$_1$) one (No. 10) we determined the energy shifts between the three spectra to be (P$_{\text{impl}}$ − C$_{\text{evap}}$) = (0.2 ± 0.2) eV and (P$_{\text{impl}}$ − C$_{\text{impl}}$) = +(1.9 ± 0.2) eV. These values agree within 3σ with those of (−(0.7 ± 0.1) and +(2.2 ± 0.1) eV [23], respectively, obtained for the rubidium KLL Auger spectra following the EC decay of $^{85}{\text{Sr}}$ in the same sources. Because of the significantly lower atomic number (and hence also much lower probability for inelastic electron backscattering resulting in reduction of the low-energy tails of electron lines), the carbon substrate would be more suitable for the super stable calibration $^{85}{\text{Rb}}$/$^{83}{\text{Kr}}$ sources in the KATRIN project than the platinum one. But the experimental data on the KLL [23] and KLM + KLN Auger electron spectra of rubidium indicate a strong influence of at least polycrystalline carbon matrix on their absolute energies in the case of implanted sources.

4.2. The energy difference of the KL$_3$M$_3$(P$_2$, $^3$S$_1$) + KL$_3$M$_3$(P$_0$) components between Kr and Rb

In the EC decay chain of the $^{83}{\text{Sr}}$ isotope (see figure 2), the KLM + KLN Auger electrons of both rubidium and krypton are also emitted. As can be seen from the insert in figure 8, the corresponding Auger electron spectra were well resolved in an overview low-energy electron spectrum taken with the $^{85}{\text{Sr}}$ source (produced by the ion implantation into the Pt foil) after about four $^{85}{\text{Sr}}$ half-lives from the source preparation. From the measured KLM + KLN spectra, a value of (713 ± 2) eV was determined for the energy difference the KL$_3$M$_3$(P$_2$, $^3$S$_1$) + KL$_3$M$_3$(P$_0$) Auger line groups between rubidium and krypton. This value agrees very well with that of (712.8 ± 2.0) eV determined from the absolute energies of the KL$_3$M$_3$(P$_2$, $^3$S$_1$) + KL$_3$M$_3$(P$_0$) Auger line groups of rubidium (obtained in the present work with the $^{85}{\text{Rb}}$ source, see table 1) and krypton (measured in [21] to be (12 409.1 ± 1.5) eV using a $^{85}{\text{Rb}}$ source prepared by evaporation in vacuum on a mirror-like Al backing).

On the other hand, a value of 723.8 eV obtained from the semi-empirical Auger-electron energy calculations [4] is higher by (10.8 ± 2.0) eV than the experimental difference. However, the semi-empirical absolute Auger-electron energies [4] for krypton are referenced to the vacuum level and are valid for the gas-phase system while those for rubidium were calculated for a solid and are related to the Fermi level. When a correction [4] to Auger-electron energies for a phase change was applied with the use of both the electron binding energies [22] for krypton generated in the matrix of the high purity polycrystalline platinum foil and a solid-state correction for rubidium [4], then a value of (12 413.3 ± 2.0) eV was obtained as the semi-empirical energy of the KL$_3$M$_3$(P$_2$, $^3$S$_1$) + KL$_3$M$_3$(P$_0$) Auger line group of krypton situated in a platinum matrix. This value is then higher by (4.2 ± 2.5) eV than the above mentioned energy [21] measured for krypton created on the Al backing but in agreement with it within 2σ. Using the modified semi-empirical value for krypton in a solid matrix, a difference of (707.3 ± 2.0) eV is obtained for the energy difference of the KL$_3$M$_3$(P$_2$, $^3$S$_1$) + KL$_3$M$_3$(P$_0$) Auger line groups of rubidium and krypton, i.e. lower by (5.7 ± 2.8) eV than the measured one in the present work.

It should be noted that a difference of the semi-empirical KL$_3$L$_3$(D$_2$) Auger-electron energies [4] between krypton and rubidium was found to be higher by (9.5 ± 0.8) eV [22] than the experimental value for the same $^{85}{\text{Sr}}$ source, i.e. by almost the identical value as in the present work for the KL$_3$M$_3$(P$_2$, $^3$S$_1$) + KL$_3$M$_3$(P$_0$) Auger line group.

4.3. Transition intensities

The measured intensities of the resolved components of the rubidium KLM + KLN Auger-electron spectrum are presented in table 2. They are related both to the total intensity of the KLM + KLN spectrum (Σ(KLM + KLN)) and the full intensity of the ΣKL$_1$M$_1$L$_1$ line group (ΣKL$_1$M$_1$L$_1$). In addition, experimental KLM + KLN transition intensities [21] for the nearest neighbor element Kr (Z = 36) are also presented in the table since the Auger transition rates vary slowly with Z. Experimental data are compared with results of the relativistic calculations [2] in jj-coupling scheme, the non-relativistic calculations [5] in intermediate coupling (covering only the KL$_1$M$_1$L$_1$ transitions), and the present calculations. (Results of the non-relativistic calculations [3] are not involved in the table because their results were found [5] to be less reliable than those of [5] for some transitions.)

Very good agreement is seen (within 1σ) between experimental transition rates for Rb and Kr in the case of the well separated spectrum lines including the most intense ones (fitted components Nos. 7 and 9). In the case of the close-lying unresolved spectrum lines (like the fitted components Nos. 2, 3 and Nos. 5, 6), the agreement within 1σ is observed for their summary intensities. So it can be concluded that transition intensities of the rubidium and krypton KLM + KLN Auger electron spectra fit well with each other.

A comparison between the theoretical results and the experimental data indicates that the relativistic calculations ([2] and the present work) reproduce better the measured intensities for the KL$_1$M$_1$ and KL$_1$M$_2$,L$_2$ lines than the non-relativistic ones. Contributions from the relativistic effects that are particularly pronounced [64] in the K Auger transitions leading to one or two s-vacancies (in any shell) may explain this finding. The relativistic calculations [2] based on jj-coupling are, however, unsuccessful in intensity description.
for the dominant fitted components (Nos. 7 and 9). While the predictions of both the non-relativistic calculations [5] and the present calculations in intermediate coupling scheme for these two components agree with the experimental data within 2σ, the relativistic jj-coupling values [2] are lower by 4σ.

It is known (see, e.g., [65]) that intensities of the KL3M2,3, KL2M2,3, and KL3M3 Auger transitions are very sensitive to the coupling of angular momenta used in the calculations. Because the calculations [2, 5, this work] differ in considering the relativistic effects, we followed a recommendation [64] and compared theoretical and experimental values for the KL3M2,3/KL2M2,3 transition intensity ratio in order to investigate the spin–orbit coupling effect on the rubidium KLM Auger electron spectrum. It was shown in [64] that while the KL2,3M2,3 transition intensities are negligibly influenced by the relativistic effects, the KL3M2,3/KL2M2,3 transition intensity ratio is very sensitive to the coupling type. As can be seen from table 2 (the last row) and figure 1 (the open circle) that the KL3M2,3/KL2M2,3 intensity ratio derived from the intermediate coupling calculations [5, this work] agrees with the experimental value within 1σ while the jj-coupling prediction [2] differ from it by 17σ. It is, moreover, seen from figure 1 that in order to find the upper limit for the atomic number Z where the intermediate coupling scheme should be used in the KLM transition rate calculations, new and precise experimental data on the KL3M2,3/KL2M2,3 transition intensity ratio for atoms with Z lower than 37 are especially required.

The above performed comparison of the theoretical and experimental KLM transition intensities leads to the general conclusion that the MCDHF calculations accomplished in the present work are the most successful in the prediction of the KLM Auger transition rates for rubidium.

4.4. Natural widths of the spectrum components

Natural widths of some fitted spectrum components of the KLM + KLN Auger electron spectrum of 85Rb (measured with the 85Sr source prepared by evaporation in vacuum on the polycrystalline carbon foil) are presented in table 3. They are compared with the values obtained as a sum of the experimental natural widths of the rubidium atomic levels (participating in the individual Auger transitions) based on the data [66–68]. Reasonable agreement is generally observed between the calculated and measured values mainly due to the large uncertainties of the latter ones. This finding is somewhat surprising because all fitted spectrum components are multiplets and, moreover, some of them (e.g., Nos. 4, 7, 9, 10) are expected to exhibit [3, 4] very complicated structure. Thus, e.g., the dominant KL3M2,3 spectrum line group consists of six components [4]: the KL3M2 line is a doublet (terms 1P0, 1P2, 1S1) while the KL3M1 line is a quartet (terms 1P0, 1P2, 3D1, and 3P1). These six terms occupy an energy interval of 13.9 eV [4] in such a way that the 1P0, 1P2, and 1S1 terms are grouped in the 0.8 eV interval and the others in 7.9 eV with a gap of 5.2 eV between these two groups. According to the non-relativistic intermediate coupling transition intensity calculations [3], intensities of the KL3M2(1D3, 1P1) terms are negligible (about 2% of the total KL3M1 line intensity) and those of the KL3M1(1P0) and KL3M1(1P2) terms amount to 39% and 59% of the total KL3M3 transition intensity, respectively. Since the intensity of the KL3M2(1S1) term is also insignificant (less than 1% [3] of the total KL3M2 transition intensity), the six KL3M2,3 components are reduced to three ones. As the energies of the KL3M2(1P0) and KL3M2(1P2) terms differ only by 0.1 eV [4] (and thus cannot be resolved experimentally in principle due to their natural widths, see table 3), the KL3M2,3 line group should be seen in an experimental spectrum taken with high instrumental resolution as two lines with the following predicted ‘KL3M2’/‘KL3M1’ intensity ratios (see also table 2, the next-to-last row): 1.09 [2] (jj-coupling), 0.20 [3] (intermediate coupling), 0.38 (this work) (intermediate coupling), 0.49 [5] (intermediate coupling) or 0.25 after a ‘redistribution’ of the KL3M2,3 terms between the fitted components Nos. 9 and 10.

This conclusion is confirmed by the results of the decomposition of our spectrum (see figure 6) including the natural widths of the two fitted components (Nos. 9 and 10) into the KL3M2,3 line group which agree well with the expected values (see table 3) for the single lines without any broadening. Taking into account this finding and reasonable (within 2σ) agreements of the ‘KL3M1’/‘KL3M2’ intensity ratios obtained from the calculations based on the intermediate-coupling scheme with the experimental value of 0.28(5) for Rb (see table 2), one should state again that the KLM Auger electron spectrum must be described within the frame of the intermediate-coupling scheme. The same conclusion can be drawn from a detailed analysis of the KL2M2,3 line group.

5. Conclusion

An experimental investigation of the KLM + KLN Auger electron spectrum is very complicated due to its low intensity and high complexity. However, the low energy nuclear electron spectroscopy method for solid radioactive samples developed in our laboratory enabled us to perform a detailed analysis of the KLM + KLN Auger spectrum of rubidium (Z = 37) following the EC decay of radioactive 85Sr and 85mKr incorporated in different matrices. A general conclusion was drawn from the detailed analysis of the measured data and available theoretical results that the proper description of the KLM + KLN Auger electron spectrum for Z around 37 should still be based on intermediate coupling of angular momenta taking into account relativistic effects. To find the upper Z limit for application of this approach, new precise experimental data particularly on the KL3M2,3/KL2M2,3 transition intensity ratio (which was found to be very sensitive to the coupling type) are needed in the atomic number region 37 < Z < 60. The results obtained on energy shifts of the dominant spectrum components between different matrices clearly indicate that, among others, the choice of the host matrix for super stable calibration 85mKr electron sources for the KATRIN neutrino mass experiment plays an important role and should, therefore, be thoroughly investigated.
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