Publishable Summary for 17FUN02 MetroMMC
Measurement of fundamental nuclear decay data using metallic magnetic calorimeters

Overview

The overall objective of this project was the improvement of the knowledge of electron capture (EC) decay and subsequent atomic relaxation processes. New theoretical calculation techniques and extensive experiments using specially adapted metallic magnetic calorimeters (MMCs) were developed to determine important decay data which are relevant when studying the influence of EC decay in cancer therapy on the DNA level or the early history of the solar system as well as for primary activity standardisations in radionuclide metrology. The experimental parts were complemented with a new approach based on microwave coupled resonators (MCRs).

All objectives have been fulfilled and new and improved theoretical models describing electron capture decay spectra have been developed. Being validated against experimental data from this project and from literature, the data from these models can be used in applications that depend on electron capture decay, such as radionuclide metrology, low background experiments, or radiometric dating, just to name a few.

Need

Determining the age of the solar system or how cancer treatments damage DNA are two research areas that both rely on very precise knowledge of nuclear decay probabilities related to radioactive EC decay. Atomic data for EC decays have been derived from measurements and calculations performed more than 20 years ago, and these are now causing significant measurement problems. Compiled data, for example, were based on the frozen core approximation with no explicit description of multiple ionisation processes. Therefore, accurate experimental X-ray emission intensities were needed to establish consistent EC decay schemes and theoretical models of subsequent relaxation processes.

The precise knowledge of EC probabilities is pivotal when calculating the electron and photon emissions resulting from EC decay. The accurate knowledge of these emission spectra is a prerequisite for state-of-the-art liquid scintillation counting (LSC) techniques which are frequently used for primary activity determination in radionuclide metrology. The uncertainties of fractional EC probabilities define the resulting uncertainty of the activity determined by LSC, e.g. the triple-to-double coincidence ratio (TDCR) method. A sound improvement of the quality of LSC measurements therefore required improved computation methods of emission spectra which, in turn, could only be developed based on new theoretical approaches and experimentally determined EC probabilities of the highest achievable accuracy. In addition, X-ray emission intensities are key data used to quantify the activity of a radioactive material by X-ray spectrometry.

Some of the technical developments were carried out within the EMPIR project 15SIB10 MetroBeta for pure beta-emitting isotopes with endpoint energies in the range from 70 keV to 700 keV. To study EC decays and X-ray emissions, new developments for MMC-based techniques were carried out for high precision measurements with sources both embedded in the MMC absorber and external to the detector.

Objectives

The overall objective of this project was the improvement of the knowledge of electron capture (EC) decay and subsequent atomic relaxation processes. The specific objectives of the project were:

1. To improve experimental techniques for spectrometry using novel cryogenic detectors based on MMCs and MCRs for radionuclide metrology in the energy range of 20 eV - 100 keV.

2. To determine fractional EC probabilities of selected radionuclides by means of spectrometry based on novel cryogenic detectors with high energy resolution and very low energy threshold using sources embedded in the detector absorber.
3. To measure absolute X-ray emission intensities of selected radionuclides by using a combination of high-resolution spectrometry based on novel cryogenic detectors using external sources and accurate primary activity determination.
4. To improve theoretical models and *ab initio* calculations of the EC process and subsequent atomic relaxation and to validate them with the high-precision experimental data from this project.
5. To facilitate the take-up of the technology and measurement infrastructure developed in the project by radionuclide metrologists, nuclear physicists and other researchers.

Progress beyond the state of the art

Spectrometry by means of energy dispersive MMC detectors applied to radionuclide metrology had started some years ago. This technique had demonstrated to be particularly suitable for measurements of radioactive decay emission spectra in the energy range from a few eV up to hundreds of keV with very high energy resolution. The measurement of fractional EC probabilities required the further development of MMCs with significantly reduced low energy threshold, in the order of 20 eV.

In radionuclide metrology, MMC-based detectors had been successfully applied to high-resolution spectrometry of X-rays and gamma-rays with energies above 10 keV, typically emitted from radionuclides with high atomic number. The excellent energy resolution had allowed X-ray satellites (due to multiple-ionised states) to be distinguished; these are invisible with conventional spectrometers before. The measurement of absolute X-ray emission intensities of nuclides with low atomic number required the energy range to be extended down to 1 keV with very high detection efficiency.

Prior to the start of this project, methods to calculate EC probabilities had been mainly established for allowed EC transitions. These calculations had suffered from significant uncertainties. Improvements of the computation methods were realised within this project based on more accurate experimental data. Emission spectra of Auger electrons and X-rays are highly influenced by electron correlation leading to multiple ionisations of the atom as well as shake-up and shake-off effects. Theoretical treatment of these multiple excitations was developed for the calculation of EC spectrometry.

Results

Experimental techniques for spectrometry based on novel cryogenic detectors for radionuclide metrology in the energy range of 20 eV – 100 keV

The first objective of the project was to improve the experimental capabilities within the consortium to be able to perform the planned measurements. This included the design and fabrication of two types of MMC detectors, operated at temperatures below 0.1 K, and one MCR detector, operated below 40 K. In addition, the available low temperature environments (cryostats), other measurement infrastructure, and the radioactive source preparation techniques required improvements to reach the project goals.

The MMCs used to fulfill the second objective of measuring fractional EC probabilities were based on a 2-pixel detector design established in the predecessor project 15SIB10 MetroBeta and the chip layout was changed to improve on experimental experiences from that project, while the detector performance was identical to the previous design.

For the X-ray measurements for objective 3, a completely new MMC design was required to cover the low energy range between 1 and 10 keV with an absorption probability > 99 % in that energy range. An 8-pixel detector with a circular detection area with 2 mm diameter was developed and fabricated. To accommodate the 8 pixels, the number of read-out channels needed to be increased, which was achieved by installing the required additional wiring and without significantly influencing the base temperature ($\Delta T<1$ mK) of the cryostat.

The X-ray detector also includes an experimental setup that allows to define the solid angle for the detector and a source sampler operated at low temperatures, that allows to change the external X-ray source while the cryostat stays at operational temperatures below 0.1 K. Unfortunately, the source sampler never reached operational readiness during the project lifetime. Therefore, to perform the planned measurements, the sources were changed manually between individual cryostat cool-down cycles.

As had been known from literature and our own experience, the preparation of radioactive sources plays a major role in the outcome of the measurements. Several different approaches were tried, namely nanoporous gold as host material, laser ablation of gold surfaces before deposition, automated dispensing of *O(100)* pL droplets for precise deposition and control of the crystal growth of the dielectric source material, electrodeposition as well as auto-deposition of iodine on silver. Only laser ablation turned out not to be beneficial.

An MCR system was modelled for its microwave resonance and particle absorption properties, designed and build. After a first homodyne read-out setup did not provide the necessary performance, a second heterodyne system was designed, set up and successfully tested in conjunction with digital data acquisition.

Apart from minor experimental setbacks, the objective was successfully achieved and allowed to perform the planned measurements with only minor restriction.

Determine fractional EC probabilities of selected radionuclides by means of spectrometry based on novel cryogenic detectors with high energy resolution and very low energy threshold using sources embedded in the detector absorber

The second objective was concerned with the first set of measurements, to determine fractional electron capture probabilities of several different radionuclides. The preparation of the experiments required a selection and characterization of the radioactive materials that had to be enclosed and suitable materials, that ideally absorb all energy from the radioactive decay. These measurements were solely performed with MMCs.

Aqueous solutions of the radionuclides ^{54}Mn, ^{59}Ni, ^{65}Zn, ^{109}Cd and ^{125}I were acquired and characterised for their activity concentration and radioactive impurities before the samples were prepared and enclosed in high purity gold as absorber material. The thickness of the absorber material was determined using Monte Carlo simulations, using the code Penelope, that simulates particle absorption and transport in matter. This was done individually for each radionuclide, since it depends on the energy and type of radiation, that is emitted from the decay.

We used several different techniques to produce the samples for the final measurements. ^{65}Zn was electrodeposited onto a gold backing, ^{54}Mn and ^{59}Ni were micro-dispensed into nanoporous gold, ^{109}Cd was micro-dispensed onto solid gold, while ^{125}I was self-deposited onto a silver backing. Afterwards, the samples were enclosed in gold by diffusion welding, attached to an MMC and then measured.

World firsts were achieved in resolution and energy thresholds for these nuclides, but the quality of the outcome was still mixed. The spectra of ^{54}Mn and ^{65}Zn came out very clean and allowed a precise determination of the fractional EC probabilities, while ^{125}I was also measured well but suffered from the escape of high energetic photons. ^{59}Ni and ^{109}Cd both showed distortions in the spectrum shape, that had already been described in literature in other low-temperature detector measurements and are usually attributed to electron scattering in the dielectric source material used in these measurements.

Although to a varying degree, all measurements were successful, and the objective fulfilled.

Method to determine absolute X-ray emission intensities of selected radionuclides by using a combination of high-resolution spectrometry based on novel cryogenic detectors using external sources and accurate primary activity determination

The third objective aimed to determine X-ray emission intensities of the same radionuclides (^{54}Mn, ^{59}Ni, ^{65}Zn, ^{109}Cd and ^{125}I) using both MMCs and the MCR system. Apart from the detector development, also the source preparation plays a significant role to measure X-rays accurately to very low energies. Especially at energies below 1 keV, self-absorption in the source material itself can reduce the intensity, while Auger electrons, that are also emitted after the decay, should not reach the detector, since these cannot be distinguished from X-rays with the used detector technologies.

A stainless-steel backing was used for all X-ray sources and ^{54}Mn and ^{65}Zn were directly electrodeposited on that backing. The other nuclides (^{59}Ni, ^{109}Cd and ^{125}I) were drop deposited onto a latex pad on the backing, that allowed a more homogeneous distribution of the radioactive solution before drying.

Two different MMC systems were used for the X-ray measurements. The MMC SMX3 had already been developed, characterised, and used for several measurements before the project. This system is optimised for photon energies up to 26 keV, but its photon absorption characteristics were extensively scrutinised to ~ 60 keV using a combination of a well characterised high-energetic (E<100 keV) photon emitter (^{241}Am), accompanied by Monte Carlo simulations of the whole setup. Due to the higher energy emissions of ^{109}Cd and ^{125}I, these nuclides were well suited for measurements with the MMC SMX3 system.

The newly developed MMC for low energy X-rays below 10 keV, named MMC LEX, was successfully used to measure the remaining nuclides ^{54}Mn, ^{59}Ni, and ^{65}Zn.

The γ-rays of ^{109}Cd and ^{125}I, and the K- and L-X-rays of all nuclides could be identified in the measured spectra and analysed for their relative intensities. Only in ^{59}Ni, the L-X-rays showed a significantly reduced intensity, likely due to self-absorption in the source. The data allowed to analyse the relative X-ray intensities. Absolute intensities could unfortunately not be given, since the sample changer did not become operational in time, which prohibited an in-situ solid angle calibration, which is necessary to give absolute values.

The MCR system was used for characterization measurements, both with an alpha-emitter (^{241}Am) and microwave calibration pulses injected into the microwave resonator, which could be clearly identified and showed a duration of about 1 ms, consistent with expectations. Unfortunately, the detector performance and low-energy threshold were not good enough to significantly contribute to the X-ray measurements.

Nevertheless, even without the MCR system, the MMC measurements allowed to mostly fulfil the objective by covering all planned radionuclides. Only the non-operational sample changer led to only relative and not absolute X-ray emission intensities.

Improved theoretical models and ab initio calculations of the electron capture process and subsequent atomic relaxation and their validation with experimental data

Achieving theoretical predictions of electron capture decays and subsequent atomic relaxation processes at the percent precision level is highly challenging. This problem was tackled in the present project employing different approaches among the most precise available and comparing the results to measurements.

An improved modelling of electron capture decays was developed including refined atomic and quantum electrodynamics corrections. Important parameters related to the atomic wave functions were extensively tabulated in order to greatly speed-up the calculations. This modelling was implemented in the BetaShape code, originally developed for beta decay calculations and adopted by several international collaborations on nuclear decay data. Electron capture probabilities were compared to accurate measurements available in the literature and excellent agreement was found within the precision of the latter.

A realistic atomic model was developed within the framework of the relativistic density functional theory, in which several exchange-correlation functionals and self-interaction-corrected models among the most popular in the community were implemented. Correlation effects were studied by comparison with measured binding energies and the best model was selected to generated precise atomic wave functions. The electron capture decay modelling developed in this project was further improved by employing these wave functions, in particular thanks to an exact treatment of the effect of the vacancy created by the capture process. Theoretical capture probabilities for several transitions of interest were compared to available experimental values, highlighting the influence of the different corrections and assumptions.

The atomic fundamental parameters, such as fluorescence yields and Auger transition probabilities, of the radionuclides of interest in this project were calculated with high precision using a multiconfiguration Dirac-Fock code. A basic parallelisation of the code was developed to make tractable in the timeline of the project the calculation of the millions of X-ray and Auger atomic transitions. Influence of electronic correlations up the highest orbitals was studied. An extensive survey of existing data and calculation methods in the literature was performed and non-negligible discrepancies were reported. The most reliable theoretical results were found being from this project.

An effort to systematically reduce the uncertainty of the theoretical calculations of the K, L and M shells fluorescence yield has been pursued by account all possible energetic allowed transitions (auger and radiative) from all one-vacancy initial levels to all possible final levels (one- and two vacancies). This has been accomplished by the development of a code capable of distributing MCDF calculations to the available CPU-threads. The unpractical or even impossible (for some systems) task of considering all possible transitions for a given shell has been overcome for almost any system. Considering the uncertainty of a radiative transition and assuming that radiationless transitions have similar rate uncertainty < 1 %, we can assume that the expected uncertainties on the fluorescence yields for the K, L, and M shells of ~2 %, ~6 % and ~20 %, respectively has been achieved. This uncertainty escalates with the number of transitions, being the reason to have higher uncertainty for the outer shells.

Calculations of the electron capture spectrum for several radionuclide decays were performed with highly detailed atomic structure, Auger transitions to the dominant atomic configurations and energy dependency of state lifetimes. Satisfactory agreement between theory and experiment was reached over the entire energy range or the electron capture spectrum. Predicted values of fluorescence yield line widths were tested against different known experimental measurements. These calculations were implemented in Quanty, a freely available script language (www.quanty.org).

Therefore, the different aspects and approaches to this objective were also successful.

Impact

The project's results were disseminated in different ways. Stakeholders were identified and invited to join the first Stakeholder workshop in Saclay in October 2019 and a second virtual workshop in December 2021. A workshop was organised in Heidelberg in October 2020 for all those interested in EC spectra calculations using the Quanty program. The wide metrology community was invited to join a training course on nuclear data evaluations, organised by CEA that included the use of several nuclear data relevant software packages. A second training course on liquid scintillation (LS) counting was organised by NPL focussed on the relevance of nuclear data in LS. On ten occasions the project and its results were presented to European and International regulatory bodies. The broader scientific community was the target audience of ten articles in peer-reviewed journals, 18 oral and poster presentations held at national and international conferences and 20 additional presentations held at other external events. News and events as well as links to publications were published on the project website http://empir.npl.co.uk/metrommc/.

Impact on industrial and other user communities

Within the project, uncertainties of nuclear decay data were reduced for a variety of radionuclides. This improved the accuracy of activity standards, which are required for industrial applications. In the case of ^{41}Ca, the newly calculated EC probabilities were used to recalculate its half-life which is relevant for research related to the early history of the solar system and also for radioactive waste management. Since the calculated EC probabilities have lower uncertainties, this re-evaluation led also to a half-life with reduced uncertainty. Improved knowledge of the emission probabilities of Auger electrons and X-rays at each energy level is critical for EC nuclides used in nuclear medicine since the estimation of the administered dose greatly depends on these data.

NPL is currently reviewing its procedures for the production of γ-spectroscopy calibration sources. This has already started with ^{109}Cd and will continue for ^{65}Zn and ^{54}Mn. These sources are regularly sold to a variety of customers, and through them the improved nuclear data will increase the confidence in detector calibrations in many fields.

Impact on the metrology and scientific communities

Experimentally determined EC probabilities and X-ray emission intensities have led to improvements of theoretical calculation methods. The measured data and improved calculation methods will be an invaluable contribution to the realisation of the SI unit becquerel in radionuclide metrology. Radionuclide metrologists are now enabled to reduce uncertainties, which is important for several other fields where precise radioactivity measurements matter. This comprises geo- and cosmochronology, nuclear medicine as well as industrial applications, but also research in other fields. The improved calculation techniques of the EC process, and its subsequent atomic relaxation are essential for a sound research of radiation effects in human tissue on the DNA level. Improved calculation methods have already been presented to the "nuclear decay data evaluation community". Computed fractional EC probabilities of ^{55}Fe obtained from the BetaShape program were recommended by the Key Comparison Working Group (KCWG) of the CCRI(II) and were used by the participants of a recent key comparison on ^{55}Fe. The new EC probabilities had significant influence on the determined activity. As a result, the project already created significant impact within the radionuclide metrology community.

The developments will also contribute to new basic research experiments which require measurements of ionising radiation with high energy resolution. As an example, short baseline neutrino oscillation experiments at nuclear reactors would benefit from accurate EC probability measurements for the indispensable evaluation of background sources.

Beyond the direct impact from the measurements on EC decaying nuclides, the advances in MMC and related readout techniques triggered by this project will be highly beneficial in numerous fields of applied and fundamental research in which MMCs play an increasingly important role. Some of the developments will also be applicable to other types of cryogenic detectors, thus reaching even more fields of research and further extending the outreach of the project.

An intercomparison exercise is currently ongoing among NMIs for the standardization of ^{109}Cd. The results will strengthen/broaden our calibration and measurement capability (CMC) claims for a multitude of methods of standardization. Ultimately standardised sources will be submitted to SIR resulting in updates of KCRV for derived SI units of Bq.

Availability of electron capture probabilities

The BetaShape code, which has been further developed within this project, has been used to provide electron capture probabilities (as well as beta spectra) for a major international collaboration on nuclear decay data evaluation: the Decay Data Evaluation Project (DDEP). This collaboration provides decay scheme data to the metrology community and a large audience of users, from fundamental physics to nuclear reactor industry and nuclear medicine. The entire DDEP database has been updated and the improved data have been made freely available at: http://www.lnhb.fr/nuclear-data/nuclear-data-table/. Executables of the BetaShape code have also been made freely available for various platforms at: http://www.lnhb.fr/rd-activities/spectrum-processing-software/.

Impact on relevant standards

The project has led to improved nuclear decay data by direct measurements and by improving the theoretical calculation techniques. Hence, the outcome of this project is a valuable contribution for nuclear decay data evaluations.

The SI derived unit of the becquerel must be established for each radionuclide individually and generally requires a multitude of primary standardisation methods for each radionuclide. For several pure EC nuclides, the TDCR-LSC method is the preferred method. Within the project, it was demonstrated that more precise EC probabilities had immediate impact on the corresponding activity standards and better knowledge of the electron and photon emission spectra and intensities will lead to further improvements when standardising EC radionuclides.

Longer-term economic, social and environmental impacts

This project has accelerated innovation and competitiveness in the field of the ground-breaking technology using MMCs and more generally cryogenic detectors. Other metrology institutes are already beginning to get involved in this field, which is certainly also a consequence of the success of this project and its predecessor MetroBeta. On a long-term perspective, MMC-based detectors may become a tool for enhanced nuclear spectrometry with an energy resolution which is much higher than with any semi-conductor detector. In particular, spectrometry at very low energy, where the detection efficiency of conventional techniques drastically drops off, benefits from the outstanding low energy threshold of MMCs, enabling substantial reduction of systematic effects. Ultimately MMC detectors enable research and applications far beyond current limits which are, at present, defined by existing spectrometers based on semi-conductors. Due to the high potential of MMCs, it is anticipated that the technology will be widely used in various disciplines. The nuclear decay data which has been determined with better precision beyond this project will be important in many fields such as nuclear medicine, industry or geo- and cosmochronology.

List of publications

1. Mougeot, X.: Towards high-precision calculation of electron capture decays. In: Applied Radiation and Isotopes 154 (2019), 108884, https://doi.org/10.1016/j.apradiso.2019.108884

2. Martins, L. et al.: Multiconfiguration Dirac-Fock calculations of Zn K-shell radiative and non radiative transitions. In: X-Ray Spectrometry 49, Issue 1 (2019), 192 – 199, https://doi.org/10.1002/xrs.3089
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6. Fretwell, S. et al.: Direct Measurement of the ^{7}Be L/K Ratio in Ta-Based Superconducting Tunnel Junctions. In: Physical Review Letters 125, 032701 (2020), https://doi.org/10.1103/PhysRevLett.125.032701 and https://arxiv.org/abs/2003.04921v2
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This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:		June 2018, 36 months + 6 months
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