

# EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

## Letter of Clarification to the ISOLDE and Neutron Time-of-Flight Committee concerning Letter of Intent: INTC-2015-008, I-161

### Emission Mössbauer Spectroscopy of high energy transition isotopes

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### Abstract

The INTC has requested a clarification letter for Letter of Intent: **INTC-2015-008, I-161**, *Emission Mössbauer Spectroscopy of high energy transition isotopes*. We are pleased to note that the INTC *felt positive towards the proposal*, and we are happy to provide clarifications to the points raised by the INTC.

It should be emphasized that at this stage with our Letter of Intent, we are asking for shifts to develop the use of specific beams produced at ISOLDE produced isotopes for emission Mössbauer spectroscopy with particular applications in biophysics and solid state physics. Once the feasibility of the requested beams has been demonstrated and documented, and the experimental equipment demonstrated to work, producing data in a reliable and reproducible way we expect that proposals on specific applications will be submitted to the INTC.

**Requested shifts:** 4 shifts, (split into ~4 runs over ~2 years)



### Points raised by the INTC:

In the following we address the issues raised by the INTC.

- (i) *A clear motivation for the extension to higher energy isotopes. The authors present a variety of different applications without specifying what they want to learn in detail.*

Since we seek to develop the method of emission Mössbauer spectroscopy at ISOLDE, it is admitted that we did not give significant details on the potential applications and the uniqueness of the possibilities that will emerge with the usage of these beam in the Letter of Intent. With this Clarification Letter we can specify this in greater depth.

Currently our collaboration utilizes with success isotopes that decay to the Mössbauer states of  $^{57}\text{Fe}$  (14.4 keV) and  $^{119}\text{Sn}$  (23.9 keV). This limits us to only cover a fraction of the periodic system. By making use of more isotope transitions, we can study materials/dopants in a wider context than now possible.

Another limitation of the two radioactive isotopes currently available at ISOLDE is due to the lifetime of the parent isotopes applied ( $^{57}\text{Mn}$ : 1.45 min. and  $^{119}\text{In}$ : 2.4 min.) which imposes constraints on post-implantation annealing of samples and experimental conditions during measurements.

The main potential of the new Mössbauer probes we seek are, among others, lifetimes of more than 1 hour, up to 65 hours. The longer lifetime of the parent isotopes allows for more complete post processing of samples, such as annealing studies, and measurements under different conditions (e.g. illumination or external magnetic field) and different (bio)chemical sample preparation (e.g. implant into ice).

In some cases, we are interested in the chemical properties of the Mössbauer parent/probe atoms, where we want to apply parents/probes that are relevant for the system under study ( $^{197}\text{Hg} \rightarrow ^{197}\text{Au}$  and  $^{61}\text{Cu} \rightarrow ^{61}\text{Ni}$  emission Mössbauer spectroscopy on e.g. (bio)chemical systems) or we want to make use of the Mössbauer probe to gain insight into the intrinsic properties of the host material (vacancy trapping at metal sites, annealing kinetics etc.). In the latter case, it is beneficial to make use of Mössbauer probes with high sensitivity of the specific interaction in question.  $^{166}\text{Er}$  has a large electric nuclear quadrupole moment for the  $2^+$  Mössbauer state making determinations of site symmetries easy.  $^{61}\text{Ni}$  has great details within the nuclear magnetic hyperfine interaction, due to the  $5/2$  to  $3/2$  transition. Both types of studies mentioned above motivate us to extend and use of larger part of the periodic system.

The addition of new isotopes to our suite of probes will thus considerably increase the possibilities in the applications of emission Mössbauer spectroscopy at ISOLDE and further strengthen this unique technique and our position within this field.

Further specifics of the scientific motivation are addressed in point 2) under (ii).

(ii) *What is the unique piece of information that the authors want to obtain from their studies, compared to other techniques?*

This is addressed in a twofold way: First we point out the unique information that is obtained with emission Mössbauer spectroscopy. Second we discuss how the information obtained relates to the studies that were suggested in the Letter of Intent.

### **1) Uniqueness of emission Mössbauer spectroscopy:**

By means of Mössbauer spectroscopy, one obtains (amongst others) unique information on the valence/spin state of the probe through the isomer shift, local site symmetry of the probe through the nuclear hyperfine quadrupole interaction, magnetic interaction through the nuclear magnetic hyperfine interactions and relaxation effects (e.g. spin relaxations, diffusion, electron hopping...) on the timescale comparable to the lifetime of the Mössbauer state, through e.g. temperature dependent broadening of spectral features.

Other methods can give complementary information, such as perturbed angular correlation (PAC), electron paramagnetic resonance (EPR) and extended X-ray absorption fine structure (EXAFS), however, the sensitivity of the Mössbauer technique allows detecting up to five different probe sites or properties (spectral components) and is not affected significantly by a distribution of environments, which makes the technique unique and powerful.

Emission Mössbauer spectroscopy allows us to make measurements on highly dilute samples (implanted to fluences less than  $10^{12}$  atoms/cm<sup>2</sup>, corresponding to local concentration below  $10^{-3}$  at.%. This has three significant consequences in comparison with methods using stable isotopes.

1: The concentration limit is well below the amorphization threshold of host materials (typically  $10^{13}$ - $10^{14}$  atoms/cm<sup>2</sup> depending on the material). At fluences below  $10^{13}$  atoms/cm<sup>2</sup>, the implanted probe atoms come to rest in amorphous zones (typically few nm across) which anneal (recrystallize) at considerably lower temperatures than amorphous layers. Among the best examples of this typical behaviour, is the case of silicon, where amorphous zones anneal below 200°C, while amorphous layers need typically annealing temperatures above 1000°C (see e.g. discussion in [Gunnlaugsson02, Weyer03]). Similar results have been observed on other materials we have studied.

2: Due to the low concentration of probe atoms and reduced annealing temperatures, we do not have to worry about precipitation, which affects the results obtained by many other techniques.

3: Interaction between probe atoms is avoided. For example, dipolar interaction between magnetic ions starts to take place at  $\sim 10^{-2}$  at.% meaning that with emission Mössbauer spectroscopy we can for example determine spin-lattice relaxation rates of the pristine lattice environment.

## 2) Unique information on the systems under study:

### 2.1. Biological studies

The aim of the bio-applications is first of all to establish a proof of concept that such experiments are feasible. This is to be achieved with samples where the local structure at the probe site and nuclear quadrupole interactions are known e.g. Hg(II) binding to TRI peptides, CuO<sub>2</sub>, and the protein azurin. The latter experiments (on azurin) will additionally move the project further and beyond the proof of concept, giving novel and unprecedented characterization of the local metal site structure of both the reduced (Cu(I)) and oxidized (Cu(II)) state. This is interesting because it is generally assumed that the structure at the metal site is similar for the two oxidation states, thus reducing the reorganisation energy of the protein embedding the metal ion upon reduction/oxidation, and facilitating electron transfer. However, this assumption has not been fully substantiated experimentally.

Mössbauer spectroscopy may elucidate whether this assumption is valid, because both the oxidation state may be observed (via the isomer shift) and the nuclear quadrupole interaction may be determined and compared for the two oxidation states, reflecting similarities or differences in structure. Other techniques such as X-ray diffraction suffer from the risk of reducing Cu(II) to Cu(I), and thus it is difficult to know with certainty the oxidation state during the structure determination, and NMR spectroscopy is only feasible on the reduced state, as the paramagnetic Cu(II) gives rise to rapid nuclear spin relaxation.

Finally, it will be straight forward to include additional research projects beyond the scope of establishing proof of concept. Such experiments are not described in the current Letter of Intent, but to demonstrate that we have them in the pipeline, three examples of systems, (which we are exploring using other techniques, i.e. we have the necessary expertise to handle them) could be 1) to elucidate how the natural Cu(I) sensor protein CueR selectively responds to monovalent metal ions and not to divalent metal ions by measuring the nuclear quadrupole interaction of Cu(I) bound, 2) to characterize different metal site structures in the process of transferring Hg(II) from one so-called HAH1 protein to another, as a prototypical example of metal ion transport, or 3) to characterize the oxidation state and metal site structure of Cu at different states of the catalytic cycle of the cellulose degrading enzyme GH61 relevant to the production of biofuels.

### 2.2. Dilute Magnetic semiconductors

In the study of dilute magnetism, two properties make emission Mossbauer spectroscopy unique. First the possibility of measuring in the truly dilute regime ( $<10^{-3}$  at.%), where e.g. spin-spin relaxations do not apply, and second to make use of the lifetime of the Mössbauer state of the probe (here specifically <sup>61</sup>Ni) to measure spin-relaxation times.

Apart from contributing to the on-going search of dilute magnetic systems (see Letter of Intent), we have encountered a discrepancy between theory and experiments on spin-relaxation times. By means of <sup>57</sup>Fe emission Mössbauer spectroscopy from implantation of <sup>57</sup>Mn, we have observed unusually slow spin-lattice relaxation rates in ZnO [Mølholt12] and

TiO<sub>2</sub> [Gunnlaugsson14] not predicted by theory. Apparently, something is missing in the theoretical description of these materials, and this motivates us to study this further. Use of other probes will allow us to further investigate this behaviour at time scales not reachable with <sup>57</sup>Fe isotope.

### 2.3. Heusler alloys

The multifunctional properties that these alloys exhibit, as magnetocaloric effect, the magnetoresistive effect and the shape memory effect, are mediated directly by the martensitic transformation. The temperature at which this transformation takes place, depends critically on the degree of crystalline order and on the composition. Therefore, the modification of these two factors shifts the temperature in which martensitic transformation occurs, that can be optimized for future applications.

The Mössbauer probe nucleus <sup>61</sup>Ni obtained from long lived parent isotopes (several minutes) gives the great possibility of performing site selective doping in Ni<sub>2</sub>Mn based Heusler alloys, which will give unique information about the Ni surroundings and the Ni influence (particularly the interplay with Mn atoms) on the magnetism of these alloys in stoichiometric and non-stoichiometric conditions. The Mössbauer study of <sup>61</sup>Ni in Ni<sub>2</sub>Mn based Heusler alloys, would complete the study currently underway within the project IS578 in which <sup>57</sup>Mn and <sup>119</sup>Sn are used. It will give the unique possibility of studying the Ni role in the martensitic and ferromagnetic transformation.

The implantation and the following Mössbauer study of <sup>61</sup>Ni in these alloys, will allow the unique opportunity to perform site selective doping and to obtain unique information about the Ni surroundings. This technique also allows to investigate how the implantation-induced compositional change, affects the magnetic properties of these alloys in a diluted regime (10<sup>-3</sup> at%). Moreover, it also allows studying the effect on the multifunctional properties of the implantation-created disorder around the probe atom, in which Mössbauer technique provides unique information.

In conclusion, Mössbauer spectroscopy will give a unique chance to study the combined effect of both deformation and the site selective doping in the magnetic and multifunctional properties in Ni<sub>2</sub>Mn based Heusler alloys. The use of long lifetime parent isotopes (several minutes), also provides a unique chance of studying and performing offline annealing treatments and characterization that with <sup>57</sup>Mn and <sup>119</sup>Sn can not be studied.

### 2.4. Doping with rare earth metal ions

Materials doped with rare earth ions have attracted considerable attention for photonic devices. Rare earth (4f<sup>n</sup>5s<sup>2</sup>5p<sup>6</sup>, n=0–14) are usually trivalent ions and their unique optical properties arise from the fact that their 4f inner shell is partially filled and are shielded by the 5s and 5p electrons and, hence, their luminescent energy levels do not substantive deviate when doped into different materials.

We want to investigate non-linear optical properties (e.g. up- and downconversion) of rare earth doped materials. Among the more promising host materials for the upconversion process by Er<sup>3+</sup> doping are TiO<sub>2</sub> and ZnO, systems we are familiar with from <sup>57</sup>Fe emission

Mössbauer studies, where unusual long spin-relaxation rates are observed. This may suggest that factors regarding the phonon spectra in the two metal oxides are not taken into account by theory and that this behaviour could partly be linked to the underlying physics of efficient upconversion properties. For emission Mössbauer spectroscopy on Er-doped upconversion host materials,  $^{166}\text{Er}$  (obtained with e.g. implantation of  $^{166}\text{Ho}$ ) is the perfect probe atom match to study the Er lattice sites properties which is not accessible for most other techniques.

Upconversion by  $\text{Er}^{3+}$  in thin-film Si solar cell applications, for efficiency boost, is particularly applicable as it absorbs in three bands in the infrared part of the spectrum (780–820 nm, 960–990 nm, and 1480–1590 nm) and emits upconverted photons in the distinct absorption range (500–800 nm) which is within the optimum wavelength of low-cost second generation amorphous Si solar cells. Likewise our group is also familiar with Si systems from  $^{57}\text{Fe}$  emission Mössbauer studies.

## 2.5. Studies on multiferroics

Compounds that display multiferroicity are few, since ferromagnetism and ferroelectricity are generally mutually exclusive or very weakly coupled [Hill00]. Among such compounds, R-Fe-O compounds (with R=Lu, Er, ..., rare earth element), recently attracted interest as potentially new multifunctional materials, where coexistence of ferroelectricity and magnetic ordering has been reported also in polycrystalline materials [Ikeda15].

Application of emission Mössbauer spectroscopy following implantations of  $^{166}\text{Ho} \rightarrow ^{166}\text{Er}$  into Er-Fe-O multiferroics gives unique local atomic information at Er sites, such as electronic and magnetic configurations, thus enabling a comprehensive chemical-structural-magnetic characterization at the atomic-scale. This is needed to establish a direct link between local structure and magnetism and also the macroscopic structure and functionality of the Er-Fe-O compounds.

*(iii) Moreover, the presented scientific motivation for the solid state physics applications was found rather weak.*

The “weakness” of the scientific motivation should have been addressed above. Several other points were raised under (iii) and will be clarified one by one.

*[a)] In dilute magnetic semiconductors (DMS) it is well known that the magnetic properties are very sensitive to sample preparation. The implantation of a heavy isotope usually generates damage and disorder at its stopping site – and one won't get intrinsic information about the DMS but rather information about the disturbed local environment of the isotope.*

For certain materials, the implantation process is indeed a problem. The important point here is that the measurements are on samples implanted below the amorphization limit ( $<10^{12}$  at./cm<sup>2</sup>) where the recovery of the lattice takes place at much lower temperatures than amorphous layers (see discussion under point (i)).

*[b)] Annealing is necessary and might overcome some of these problems, but the short isotope lifetimes are a limiting factor for the entire approach.*

In the case the implantation process is a problem, the idea with the new isotopes with longer lifetimes is exactly to anneal the sample before measurements. The lifetime of the isotopes proposed here are above 1 hour, which makes high temperature implantations and post annealing easily possible.

*[c)] In the published work the authors only reported on non-magnetic systems, usually with very low concentration of magnetic impurities ( $10^{-4}$  at %; it seems that uncharacterized samples were used, which is a weak point for this kind of studies).*

In our studies we apply either the best material (single crystals) available commercially (and therefore heavily characterized) or collaborate with groups where they have or are in the process of characterizing the samples with macroscopic methods. This statement is not relevant for the Letter of Intent.

*[d)] However, DMS show ferromagnetic order only in the % range. It would have been much more interesting to study a system where it is known that ferromagnetic order is present.*

This is something we have indeed studied with  $^{57}\text{Mn}$  isotope, please see [Mantovan et al. <http://dx.doi.org/10.1002/aelm.201400039>], and not relevant for the current Letter of Intent.

*[e)] Another problem is that today's DMS research focuses on materials which are magnetic at room temperature: with the new proposed isotopes room temperature is not accessible, although it would be interesting to study the material in the ordered and in the paramagnetic state.*

Ferromagnetic to paramagnetic transitions are best studied with macroscopic methods (magnetization). We want to emphasize on the nature of atomic-scale magnetism with truly dilute local probe methods. This addresses questions on valence/spin state of the probe atoms and local symmetry. Where applicable, pre-doped samples are used, but this is beyond the scope of the current letter of intent.

*[f)] With the information provided in the proposal the Committee didn't see the scientific impact of such a study. This applies also to the other proposed topics where the authors remain vague about the goals and the unique kind of information they want to obtain from the studies.*

We believe that the concerns addressed by the INTC have now been clarified in the text above. In summary, strong science cases exist for the development of new high emission energy isotopes for emission Mössbauer Spectroscopy at ISOLDE/CERN, with applications in bio-sciences and solid state physics. The uniqueness of the expected information springs from the uniqueness of the emission Mössbauer spectroscopy technique which utilizes extremely low fluence implantations of probe Mössbauer isotopes that are below the detection limit of other interrogation techniques. With these new isotopes added to our disposal the capabilities of emission Mössbauer spectroscopy will greatly enhance the applied nuclear program at ISOLDE.

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