

Mag Lab establishes Mössbauer spectroscopy facility

Andrew Ozarowski, Magnet Lab, Yarilyn Cedeño-Mattei, Department of Chemistry-Chemistry of Materials, University of Puerto Rico-Mayaguez

A Mössbauer spectroscopy laboratory is under development at the Mag Lab. Made possible by a User Collaboration Grants Program (UCGP) award to Andrew Ozarowski, the lab will ultimately become part of the lab's user program.

The main instrument, delivered several weeks ago, can currently take spectra only at room temperature. The low-temperature equipment should be operational by the end of June and further development includes installation of a superconducting 9 tesla (T) magnet (that can be pushed to 12 T) to study magnetically perturbed spectra.

Since Mössbauer spectroscopy is not commonly known among Magnet Lab scientists, we will explain its principles and present the first practical results obtained by Yarilyn Cedeño-Mattei, a Ph.D. candidate from Puerto Rico, who is visiting the Magnet Lab.

THE PRINCIPLE

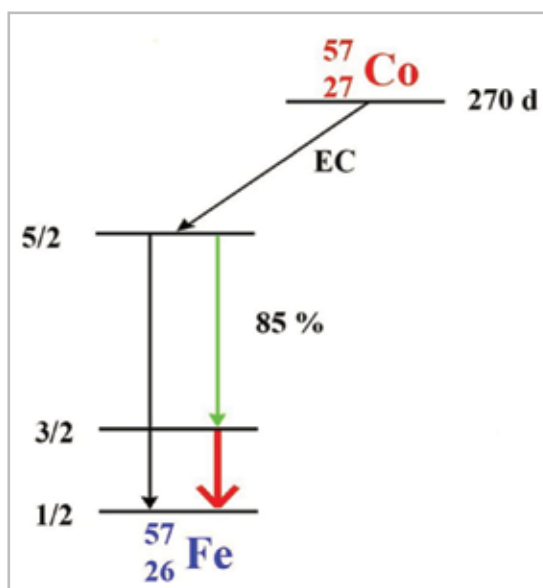


Figure 1.

Nuclear processes occurring in a Mössbauer source. The figure was taken from "Mössbauer Spectroscopy – Principles and Applications" by Philipp Gütlich, available at http://ak-guetlich.chemie.uni-mainz.de/Moessbauer_Lectures_web.pdf

In a radioactive source, Co-57 atoms undergo a nuclear "electron capture" process resulting in the formation of Fe-57 nuclei, which are born in their excited state with nuclear spin $I=5/2$. Next, the excited state energy is emitted in two steps, one from $I=5/2$ state to $I=3/2$ and finally from $I=3/2$ to $I=1/2$ state. In the latter step, a gamma quantum with energy of 14.4 keV is emitted

RECOIL-FREE GAMMA EMISSION

Emission of a gamma quantum by a free iron atom causes a recoil effect, according to the principle of the linear momentum conservation. As a result, an iron atom attains kinetic energy of

$$E_{\text{recoil}} = E_{\gamma} / 2m_{\text{Fe}} c^2$$

and the nuclear decay energy would be partitioned between E_{recoil} and E_{γ} . However, if the iron atoms are tightly bound in a crystal lattice, the recoil energy is not taken by the iron atom that undergoes gamma decay, but is rather transferred to the lattice phonons. A certain fraction (Debye-Waller factor) of the nuclear decay occurs without the lattice phonon excitation, which is essentially equivalent to the recoil momentum being absorbed by the entire crystal rather than by a single iron atom. Accordingly, the recoil energy becomes negligible resulting in unprecedentedly narrow emission band width of $4.6 \cdot 10^{-9}$ eV, some

13 orders of magnitude less than the gamma quantum energy itself. The Mössbauer effect relies on that extraordinarily monochromatic 14.4 keV radiation

GAMMA RAY ABSORPTION

When a sample containing iron is exposed to the 14.4 keV radiation, the quanta may be absorbed by Fe-57 nuclei (2.2% abundance in natural iron). But because iron atoms in the sample and in the source are in general in different environments, the Fe-57 nuclei in the sample require radiation frequency somewhat different from that emitted by the source. The frequency adjustment is accomplished by taking advantage of the Doppler effect. The radioactive source is moved versus an immobile sample and the plot of gamma absorption versus the source velocity is called a Mössbauer spectrum. Perhaps the most amazing aspect of the phenomenon is the required velocity – it is of the order of just millimeters per second.

An overwhelming majority of the Mössbauer studies are performed on iron, because of its abundance and importance in the living and non-living nature. However, the effect has been observed in more than 40 other elements including potassium, nickel, zinc, tin, gold and uranium.

IMPORTANT APPLICATIONS

- Iron detection, recognition of minerals containing iron
- Determination of the iron valence state, structure and bonding of compounds
- Magnetic properties of compounds and alloys, internal magnetic field detection and determination in ferromagnets.

Many branches of science take advantage of the Mössbauer spectroscopy, including chemistry, biochemistry and geology.



Figure 2.

Two miniature spectrometers designed in Prof. Philipp Gütllich's laboratory in Mainz, Germany were mounted on the rovers Spirit and Opportunity and sent to Mars where they identified some iron-containing minerals. Prof. Gütllich is a co-principal investigator in Ozarowski's UCGP grant. The picture was taken from http://ak-guetlich.chemie.uni-mainz.de/Moessbauer_Lectures_web.pdf

INTERACTIONS AFFECTING MÖSSBAUER SPECTRA

- Isomer shift – due to the electron density on a nucleus; provides information of the oxidation state, spin state, covalency and electronegativity. It shifts a resonance on the velocity scale without splitting it.
- Electric quadrupole interaction between the nuclear quadrupole moment and the electric field gradient on the nucleus – depends on oxidation and spin state and on the site symmetry. Splits a resonance line in two.
- Zeeman interaction between the nuclear spin and magnetic field – monitors magnetic properties like ferromagnetism. Causes six Mössbauer resonances to appear.

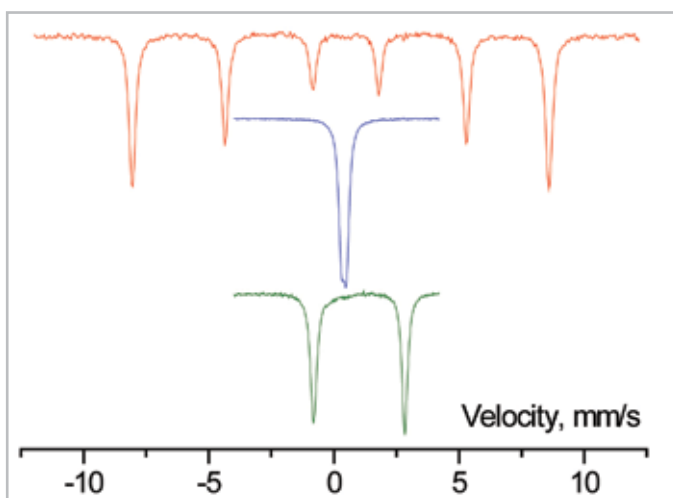


Figure 3.

Room-temperature Mössbauer spectra recorded at the Magnet Lab. Blue trace: A high-symmetry, low-spin iron(II) complex compound exhibiting a small isomer shift and very small quadrupole splitting. Green trace: a high-symmetry, high-spin iron(II) complex compound – higher isomer shift than in previous case and large quadrupole splitting. Red trace: iron(III) oxide Fe_2O_3 (hematite). Hematite is ferromagnetic and its internal magnetic field causes the Zeeman structure to appear.

PRELIMINARY RESULTS OBTAINED FOR FERRITE NANOCRYSTALS

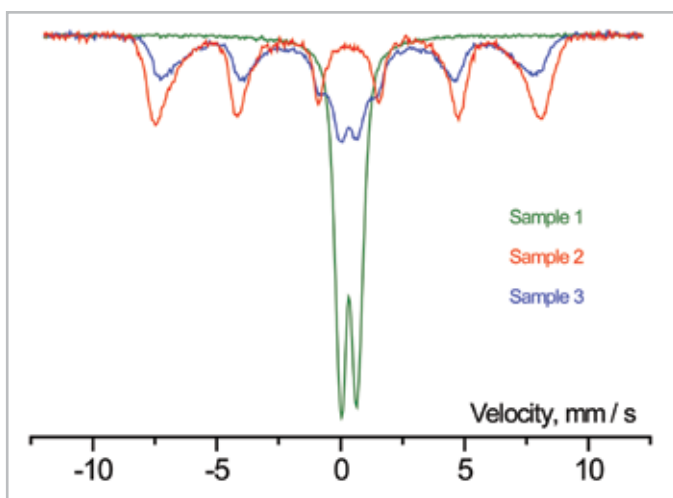


Figure 4.

Mössbauer spectra of cobalt ferrite CoFe_2O_4 nanocrystals produced by coprecipitation method under various preparative conditions to create different coercivities. Sample 1 appears to be a pure non-ferromagnetic substance, while sample 2 is a pure ferromagnetic material. Spectrum of Sample 3 is a sum of 15% of the non-ferromagnetic fraction, identical to Sample 1, and 85% of a ferromagnetic material, which is however different from Sample 2.

Yarilyn's research project titled "Composition- structure and size/shape-controlled synthesis and characterization of high coercivity ferrite nanocrystals" has as a main objective the determination of the single domain and multi-domain region limits as a function of the composition, structure, and crystal size in ferromagnetic ferrites.

The nanoparticles of cobalt-containing ferrite, CoFe_2O_4 , display unusual properties making it a desirable material for advanced technological applications ranging from biomedical treatments to magnetic storage. High coercivity, strong uniaxial anisotropy, and a moderate magnetization, in addition to its high chemical stability and mechanical hardness make this ferrite a promising candidate for magnetic recording applications. Strong dependence of coercivity on crystal size is well known, and an increase of the crystal size within the single domain region limits causes coercivity enhancement. The coprecipitation method was employed in the production of these ferrites. Several synthesis parameters have been varied to control particle size, ion distribution, and hence, the magnetic properties.

Cobalt ferrite is an inverse spinel with Fe^{3+} ions in tetrahedral sites aligned anti-parallel to those from octahedral sites. The resultant saturation magnetization comes from Co^{2+} ions located in the octahedral sites. Some studies have shown that Co^{2+} ions can occupy both tetrahedral and octahedral sites, thus the spinel may be not completely inverse.

Mössbauer spectroscopy is a useful technique that helps in the determination of the magnetic structure of Fe ions and atomic re-arrangements (cation distribution within tetrahedral and octahedral sites) in the ferrite structures. It will also provide quantitative information related to the ferromagnetic and non-magnetic (superparamagnetic or paramagnetic) fractions in the sample.

The Mössbauer spectra of CoFe_2O_4 ferrite nanocrystals in Figure 4 show that ferromagnetic, non-ferromagnetic species as well as mixtures of both were created depending on the synthetic conditions. The internal field in the CoFe_2O_4 ferrites estimated from spectra in Figure 4 is about 48 T, compared to 51 T in hematite. Also, comparison of the spectra of the ferromagnetic ferrites with the hematite spectrum (Figure 3) indicates that the internal field in ferrites under study here is non-uniform, as judged from the large linewidth in their spectra. This may indicate a distribution of the crystallite sizes.

The results presented above are very preliminary and experiments will continue, particularly after our Mössbauer instrument enhancement. For now, the spectra in Figure 4 have confirmed that the synthetic methods were successful: sample 1, whose spectrum is plotted in green has been prepared under conditions restricting crystal growth and it was expected to be superparamagnetic rather than ferromagnetic. The presence of only the ferromagnetic phase in sample 2 spectrum indicates that all crystallites must be larger than 10 nm, while the spectrum of sample 3 suggests a wider size distribution with particles both smaller and larger than 10 nm.

ACKNOWLEDGMENTS

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