Hyperfine Interact
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Fifty years of Mössbauer spectroscopy: from alloys and oxides to glasses and nanoparticles

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Abstract The Mössbauer Effect was discovered in 1957. In 1960 Mössbauer spectroscopy was born when two important papers appeared on (i) the magnetic hyperfine interaction and (ii) the electric monopole (isomer shift) and quadrupole interactions. These transformed an interesting phenomenon into a method for probing solids. Applications to magnetism, metals and alloys, chemical compounds, biological molecules, geology, archaeology and other sciences followed and are still of current interest. Two areas of research where Mössbauer spectroscopy is making unique contributions are in determining oxidation states in (i) glasses and (ii) nanoparticles. Some recent measurements are described.

Keywords Magnetism · Nanoparticles · Glasses · Mössbauer spectroscopy

1 Introduction

Mössbauer spectroscopy began with two important papers which were published in 1960, one by Hanna et al. [1] on the magnetic hyperfine interaction in ferromagnetic metallic iron, and the other by Kistner and Sunyar [2] on the electric monopole (isomer or chemical shift) and quadrupole interactions in the antiferromagnet Fe_2O_3. These transformed an interesting phenomenon into a method for probing solids. Applications to the magnetism of iron alloys (Fig. 1) and oxides (Figs. 2 and 3) followed quickly, and were extended to studies of chemical compounds and biological molecules. In addition to iron, about 20 other elements including tin, europium and

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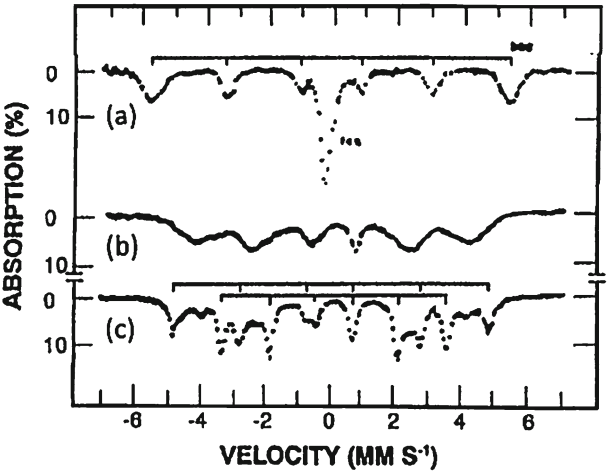

Fig. 1 Iron alloys (**a**) 32% Ni, showing bcc and fcc phases (**b**) 25% Al (**c**) ordered Fe_3Al showing two iron sites

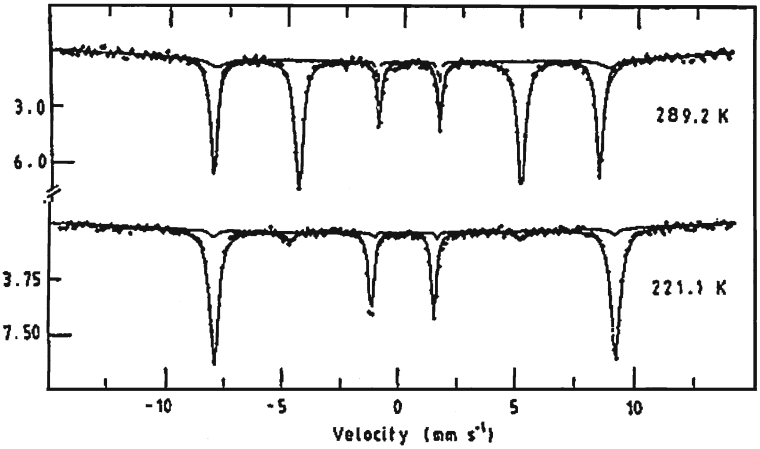

Fig. 2 α-Fe_2O_3: Morin transition. The γ-rays are parallel to the c-axis. At 260 K the spins re-orient from parallel to perpendicular to c and the electric field gradient changes sign

antimony showed the Mössbauer effect. Its use in other sciences, such as geology and archaeology, became quickly established and are of continuing interest and activity.

Although the Mössbauer effect is limited to only a few elements in the periodic table, they are important elements and unlike x-ray diffraction, which requires the periodic lattice of a crystal, the measurements do not require crystals. It is powerful in selecting the resonant isotope (e.g. ^{57}Fe) in the presence of other atoms in a sample. Furthermore through the isomer (chemical) shift it is sensitive to the charge state of the atom and so can distinguish between different oxidation states.

Mössbauer spectra, like x-ray diffraction patterns, can be used to provide fingerprints for identifying compounds or alloy phases and mixtures of them. They have been used to analyze soil and rocks from the surface of the moon and on Mars. In biochemistry some new proteins have been discovered. One of the most striking

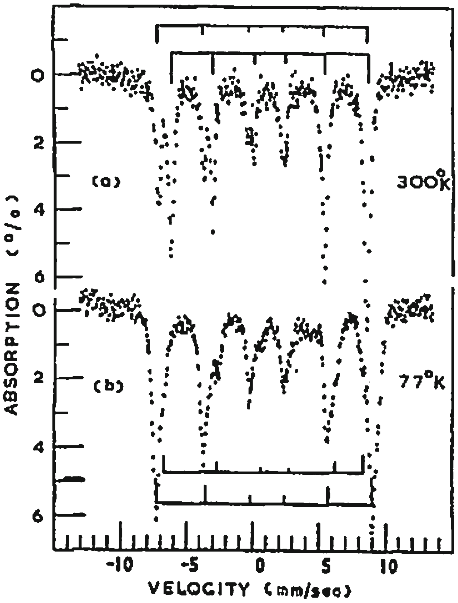

Fig. 3 Fe_3O_4: Verwey transition. At 110 K the structure changes from normal to inverted spinel

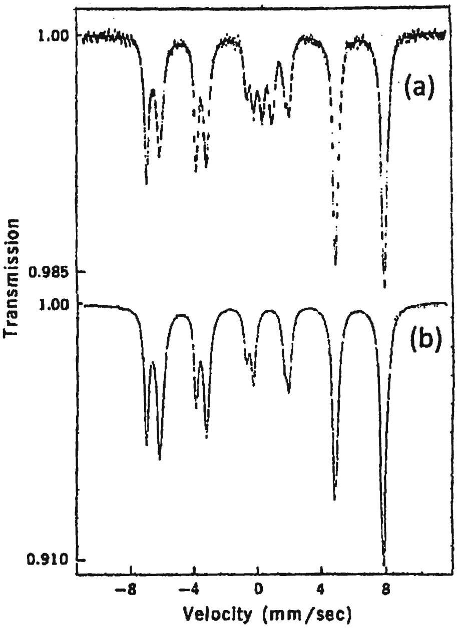

Fig. 4 ^{57}Fe spectrum at room temperature of (**a**) magnetic cells from magnetotactic bacteria *spirillum* (**b**) Fe_3O_4 [3]

examples of its use in biology was by Frankel et al. [3] who identified Fe_3O_4 in the brain of pigeons and in magnetotactic bacteria, thereby establishing that birds and bacteria navigate by sensing the earth's magnetic field. Figure 4a shows the spectrum of cells from magnetotactic *spirillum* which is seen to be similar to that of magnetite Fe_3O_4 in Fig. 4b. Subsequent electron micrographs revealed a string of Fe_3O_4 nanocrystals in the cells [3]. Among other examples of fingerprinting have been studies of magnetic phase changes [4].

Hence two areas of research where Mössbauer spectroscopy can make a unique contribution in complementing x-ray diffraction methods are (i) glasses, which only scatter x-rays incoherently, and (ii) nanoparticles, which are prone to oxidation because a large fraction of the atoms are on their surface. The ability of the Mössbauer effect to distinguish different oxidation states offers an important way of characterizing nanoparticles

Magnetic nanoparticles exhibit superparamagnetism, i.e. they are single domain and below their ordering temperature T_c their magnetic moments fluctuate rapidly so that they have a reduced net magnetization. Their Mössbauer spectra then show broadened magnetic hyperfine lines. When they are cooled below the so-called blocking temperature, T_B, given approximately by,

$$kT_B \approx aKV,$$

the fluctuations slow down and the full magnetic splitting is observed. Here V is the volume of the particles and K their magnetic anisotropy constant and a is a constant of the order of 0.04.

2 Silicate glasses

Tin and iron are both important constituents of industrial silicate glasses. Tin is involved in the float glass process which is used almost universally in flat glass manufacture nowadays. Iron is an impurity in the raw sand from which the glass is produced and is sometimes added (as also is tin) to produce glass with certain optical properties. Both these atoms can exist in different valence states and Mössbauer spectroscopy has been used to determine them.

Float glass is made, as the name suggests, by floating a moving ribbon of molten glass on liquid tin. Some of the tin diffuses into the surface and it is important to know the chemistry involved. Figure 5 shows data of Williams et al. [5] who measured ^{119}Sn spectra of slices at different average depths from the surface. It is seen that at the surface the tin is predominantly Sn^{2+} and with increasing depth the concentration of Sn^{4+} increases.

3 Iron phosphate glasses

Iron is not a glass former, but with other oxides can form glasses and usually exists in more than one valence state. For example iron phosphate glasses, a possible candidate for storing nuclear wastes, is produced by melting Fe_2O_3 and P_2O_5 and always contains some Fe^{2+}. Ray et al. [6] investigated the effect of temperature and time on the composition of these glasses. Some more recent spectra (Smith et al., private communication) are shown in Fig. 6. Both Fe^{2+} (shift 1.4 mm/s) and Fe^{3+} (shift 0.3 mm/s) are present, with the amount of Fe^{2+} increasing with increasing temperature and time of melting.

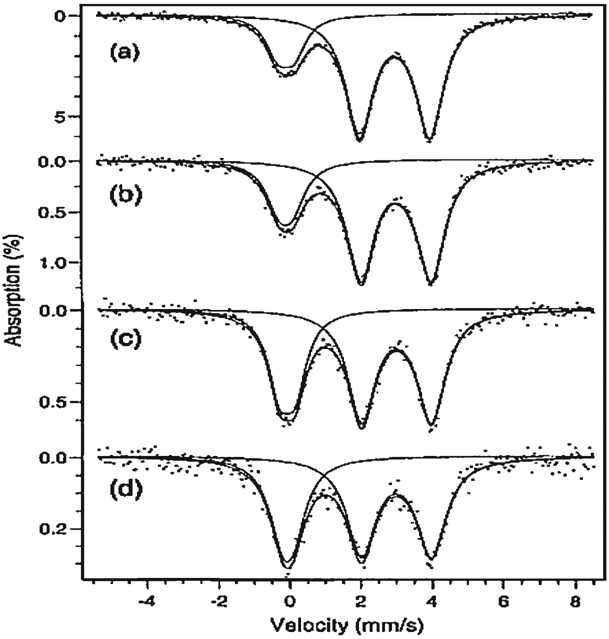

Fig. 5 ^{119}Sn spectra at room temperature of float glass slices of thickness *t* and average depth *d* below the surface (**a**) $d = 8.5\ \mu m$, $t = 17\ \mu m$ (**b**) $d = 9.25\ \mu m$, $t = 15.5$ (**c**) $t = 11.0\ \mu m$, $t = 12\ \mu m$ and (**d**) $d = 14.75\ \mu m$, $t = 4.5\ \mu m$. At the surface the tin is mostly Sn^{2+}, becoming increasingly Sn^{4+} with increasing depth [5]

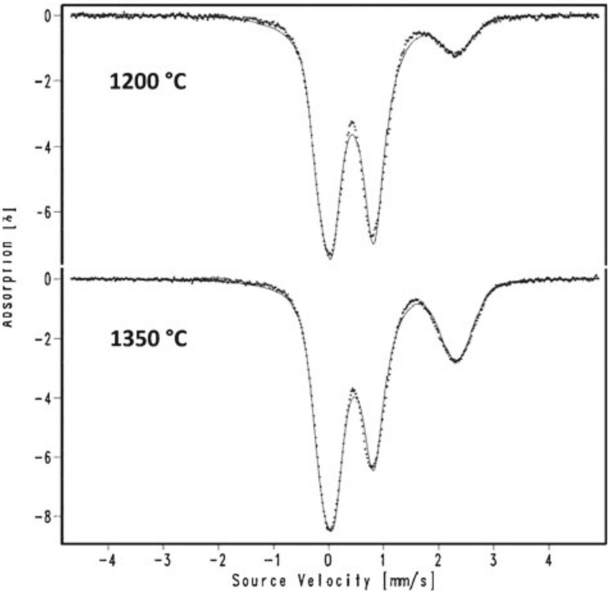

Fig. 6 ^{57}Fe spectra at 23°C of $33\%Fe_2O_3$-$67\%P_2O_5$ glasses melted at (**a**) 1200°C and (**b**) 1350°C. The fraction of Fe^{2+} increases with increasing temperature and time of melting (Smith et al., private communication)

4 Nanoparticles of iron and iron alloys

Nanoparticles of iron and its alloys are interesting because of the possibility that high temperature phases not normally stable at room temperature may be frozen in by the rapid quenching rate. They also have practical importance as they are

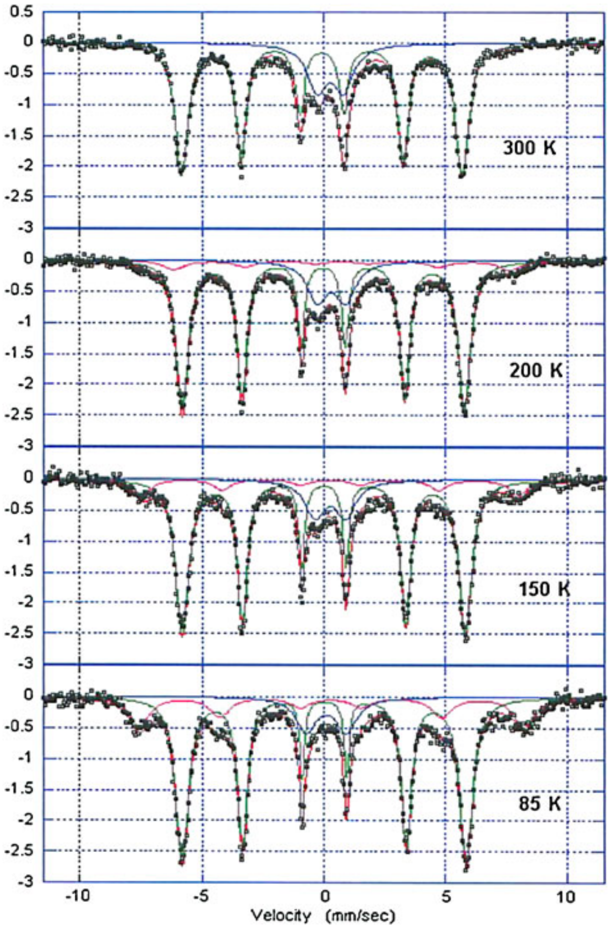

Fig. 7 ^{57}Fe spectra of 20 nm nanoparticles of $Fe_{0.5}Co_{0.5}$. The superparamagnetic oxide film on the surface becomes more apparent at low temperatures [7]

promising candidates for high density magnetic recording owing to their high saturation magnetization and coercivity. Their use may be limited by superparamagnetic fluctuations when the particle size is very small. The inevitable oxidation has a useful effect as it provides a passivating shell which protects the iron from further oxidation [7]. By reducing the interactions between the iron particles this shell can reduce the superparamagnetic fluctuations.

Mössbauer spectra (Shafranovsky et al., private communication) of 20 nm particles of $Fe_{0.5}Co_{0.5}$ at different temperatures are shown in Fig. 7. At 300 K the six lines of iron with a hyperfine field of about 34 T are seen together with a doublet arising from the superparamagnetic oxide coating where the magnetic hyperfine interactions are destroyed by the fluctuations. As the temperature is lowered the fluctuations slow down and the hyperfine lines of the oxide appear outside the iron lines with a field of about 50 T. The coating appears to contain amorphous Fe_3O_4 together with other oxides.

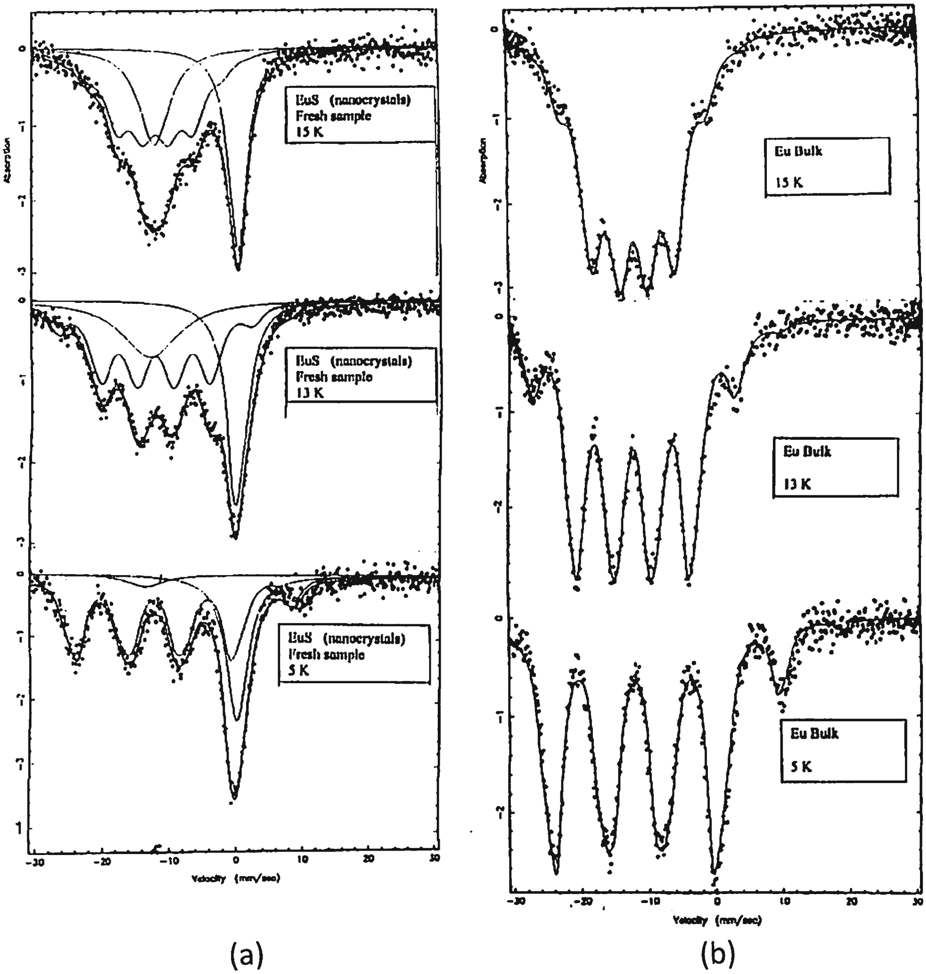

Fig. 8 ^{151}Eu spectra at 5, 13 and 15 K of (**a**) 20 nm EuS nanoparticles (note the Eu^{3+} surface impurity) compared to (**b**) bulk EuS crystals [10]

5 Nanoparticles of Europium (II) sulfide

EuS is a non-metallic ferromagnet with a Curie point $T_c \approx 18$ K. Mössbauer spectra (Dickerson et al. 2011, to be published) of EuS nanoparticles at different temperatures are shown in Fig. 8a, and may be compared with bulk EuS at the same temperatures in Fig. 8b. The spectra of the nanoparticles (Fig. 8a show that a large fraction of the europium has been oxidized to Eu^{3+}, presumably on the surface, with an isomer shift of 0 mm/s relative to the EuF$_3$ source. The Eu^{2+} line with a shift of −12.9 mm/s initially broadens as the temperature is reduced, characteristic of a superparamagnet, and eventually shows magnetic (Zeeman-like) splitting when the fluctuations have become sufficiently slow. The spectra then are similar to those of a

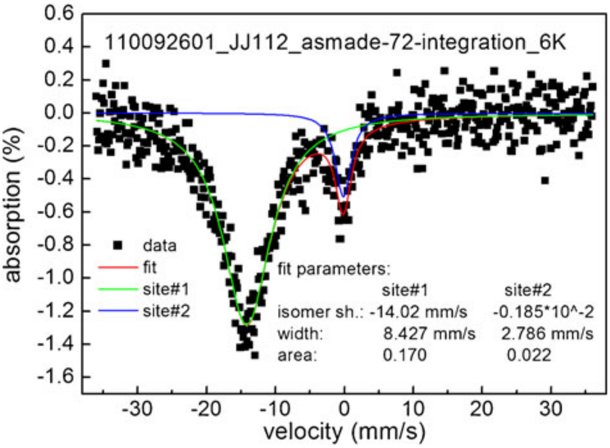

Fig. 9 ^{151}Eu spectra of Eu-doped nanocrystals of $BaCl_2$ in a matrix of a fluorozirconate glass (ZBLAN). About 90% of the Eu is in the Eu^{2+} state (Johnson et al. 2011, to be published)

ferromagnet (Fig. 8b) where the hyperfine splitting increases steadily with decreasing temperature to a saturated value (29 T) at the lowest temperature.

6 Nanocrystals of $BaCl_2$:Eu^{2+} in fluorozirconate glass

Fluorozirconate glasses based on a modified ZBLAN composition show promise as an x-ray image plate for mammography due to the extremely high spatial resolution. Upon heat treatment, these glasses precipitate $BaCl_2$ nanoparticles, which contain divalent europium. Upon x-ray irradiation electron-hole pairs are produced, which are stored until scanned by a laser. The light output is maximized by maintaining europium in the 2+ state therefore it is important to monitor the valence state of the Eu. For several years, the synthesis process has led to a roughly 50% conversion of Eu^{2+} to Eu^{3+}. However, very recent results have enabled us to document the success of maintaining 90% Eu^{2+}. Without Mossbauer spectroscopy this would have been impossible. Figure 9 is the spectrum of a sample showing this result.

7 Conclusion

It would be impossible to do justice to the wide variety of applications of Mössbauer spectroscopy in a short paper, and this is a personal, incomplete and highly selective account of some current work.

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