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3.1 Nuclear Gamma Resonance (Mössbauer) Spectroscopy

3.1.1 Summary of Theory and Important Results

F.C. HAWTHORNE

Introduction

The Mössbauer effect is the recoil-free emission and resonant absorption of γ-rays by specific atomic nuclei in solids. The γ-rays can be used as a probe of nuclear energy levels which are sensitive to the local electron configuration and the electric and magnetic fields of the solid. Thus Mössbauer spectroscopy can differentiate between oxidation states of atoms, electron spin states, and structural environments. Of particular mineralogical and petrological interest are the abilities to derive oxidation ratios and site-occupancies of elements (isotopes) sensitive to the technique.

γ-ray Emission

Radioactive isotopes are unstable and spontaneously decay by emission of radiation; γ-ray emission is one of these decay processes and is of central importance in Mössbauer spectroscopy. When a nucleus emits a γ-ray, the nucleus must recoil such that the conservation of momentum principle is satisfied. When the nucleus is part of an atom of a solid, the recoil energy is too small to break any chemical bonds, and the recoil energy transfers to the phonon spectrum of the solid. As phonons are quantized, the momentum is transferred in integral amounts, and there is a finite probability that in some cases there will be no momentum transfer. The energy of the emitted γ-ray in this zero-phonon event is equal to the energy of the transition as the emission process involves no recoil energy. If the emitted γ-ray encounters another nucleus of the same type, it can be absorbed by a zero-phonon process, raising the nucleus into an excited state. The probability of such zero-phonon events is designated the *recoil-free fraction.*

Resonant Mössbauer Absorption

In a solid, the energy levels of a nucleus are a function of its local environment; they differ from one material to another, and also from one crystallographically distinct site to another in the same material. Thus (zero-phonon) γ-rays emitted by one material will not necessarily be absorbed by another material with the same type of isotope present. However, we can modulate the energy of an emitted γ-ray by vibrating the *source* material, thus applying a continuously varying Döppler shift to the γ-ray energy. This Döppler shift can bring the γ-ray energy into coincidence with the transition (absorption) energy of the same type of isotope in a different material; when this occurs, there is *resonant absorption*. Thus if we monitor the energy spectrum of the modulated γ-ray(s), there is absorption at an energy characteristic of the nuclear state of the active isotope in the absorbing material. The modulated γ-ray is thus a probe of the nuclear energy levels of a specific isotope in a solid.

For several reasons (e.g., unsuitable half-life, low cross-section for absorption, unsuitable decay scheme), most isotopes are not suitable for Mössbauer spectroscopy. From a mineralogical perspective, ^{57}Fe is by far the most important isotope, but ^{119}Sn, ^{121}Sb, ^{153}Eu, and ^{197}Au are also of interest.

Mössbauer Parameters

Mössbauer spectroscopy involves interactions between the nucleus and extranuclear electric and magnetic fields. These are called *hyperfine interactions*; of principal importance are *monopole* and *quadrupole interactions* and *magnetic dipole interactions.*

The electric monopole interaction arises from the interaction between the positive nuclear charge and the electric field of the surrounding electrons. This interaction shifts the nuclear energy levels (Fig. 23a) according to the details of the local electronic structure. In Mössbauer resonant absorption, one compares the relative energy levels between nuclei in a γ-ray source (emitter) and an absorber (sample). This energy difference is called the *chemical* (or isomer) *shift*, δ, and is commonly measured relative to some standard material (often α-Fe for ^{57}Fe).

The isomer shift is sensitive to any factor that affects the number and/or distribution of valence-shell electrons, and is thus a probe of oxidation state, spin state, coordination, and covalency. Only s-electrons have a finite probability of overlapping with the nuclear charge density and directly affecting the isomer shift. Thus Mössbauer-sensitive isotopes with different oxidation states involving variations in the number of valence s-electrons (e.g., ^{119}Sn, ^{121}Sb) show large differences in isomer shift (Fig. 24a). On the other hand, valency differences involving p- or d-electrons only affect the isomer shift indirectly via shielding effects, and so such isotopes (e.g., ^{57}Fe) show much smaller variations in isomer shift with valence (Fig. 24a,b). Changes in coordination (coordination number, type of ligand) affect the details of the electron arrangement of the Mössbauer-sensitive isotope, and thus affect the isomer shift. Thus isomer shift can also be a probe for these parameters; in particular, the isomer shift for ^{57}Fe is sensitive to coordination number (Fig. 24b), and this can be of particular use in the characterization of poorly crystalline and amorphous phases.

The electric quadrupole interaction involves interaction between the nuclear quadrupole moment and the ambient electric field, which leads to a splitting of

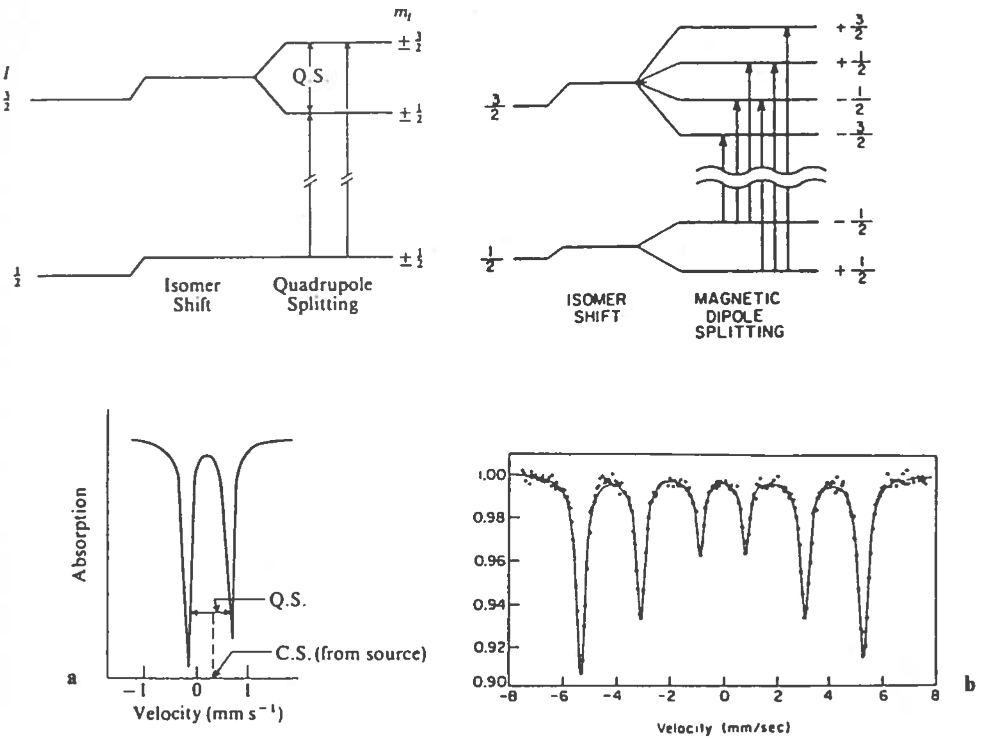

Fig. 23a,b. Nuclear energy level diagram and Mössbauer spectrum showing the combined effects of electric monopole and electric quadrupole interactions after Bancroff (1974); **b** Nuclear energy level diagram and Mössbauer spectrum showing the combined effects of electric monopole and magnetic dipole interactions, after Wertheim (1964); in both diagrams, allowed transitions are shown by *arrows*

the nuclear energy levels (Fig. 23a). This splitting is called the *quadrupole splitting* (QS) and is a function of the *electric field gradient* (EFG) in the vicinity of the nucleus. Transitions between energy levels are controlled by a set of selection rules. Each allowed transition will give rise to a single absorption in the Mössbauer spectrum. For ^{57}Fe [$I \leq (3/2)$], two transitions are allowed and a (quadrupole-split) doublet results (Fig. 23a); for ^{121}Sb (with ground and excited states of $I = (5/2)$ and $(7/2)$ respectively, eight transitions are allowed and an octuplet results. The quadrupole splitting is sensitive to details of atom co-ordination, particularly the amount of deviation from regularity.

The interaction of the magnetic dipole moment of the nucleus with the magnetic field at the nucleus further splits the nuclear energy levels, giving rise to *magnetic* (or *nuclear Zeeman*) splitting. The magnetic field removes the spin degeneracy to form $2I + 1$ energy levels (Fig. 23b). The resulting spectrum (Fig. 23b) is considerably more complex than when a magnetic field is not present. The magnetic field at the nucleus can be imposed through an externally

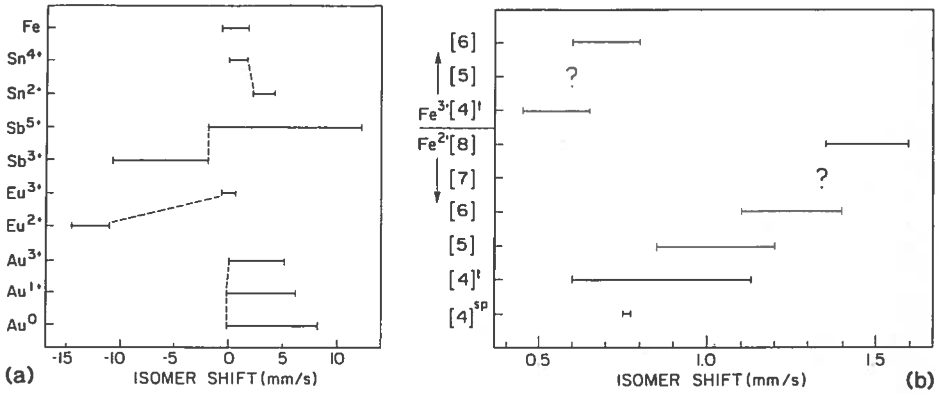

Fig. 24a, b. Isomer shift ranges for selected isotopes in various valence states: ^{57}Fe relative to Fe-foil, ^{119}Sn relative to SnO_2, ^{121}Sb relative to InSb, ^{151}Eu relative to Eu_2O_3, ^{197}Au relative to pure ^{197}Au. **a** All isotopes, note the wide range for species whose valence changes involve s-electrons (with the exception of ^{197}Au). **b** Results for ^{57}Fe, showing the effect of coordination number and valence. (After Hawthorne 1988)

applied magnetic field, or it can be intrinsic and due to unpaired orbital electrons. Thus Mössbauer spectroscopy is an important tool in the study of the magnetic properties of minerals.

Determination of Site Occupancies

The most common application of Mössbauer spectroscopy in mineralogy involves the determination of ^{57}Fe site-occupancies in minerals. In a mineral, for each crystallographically unique site partly occupied by Fe in either valence state, there will be a quadrupole-split doublet. Assuming that the recoil-free fraction of Fe is the same at each site, the relative intensities of the doublets give the relative amounts of Fe (Fe^{2+} and Fe^{3+}) at the different sites, provided the total Fe content of the mineral is known from a chemical analysis. Such results play a significant role in thermodynamic modeling of minerals.

3.1.2 Experimental Techniques and Spectrum Fitting

F.C. Hawthorne, A.V. Bykov, N.N. Delyagin, and V.I. Nikolaev

The experimental set-up of a Mössbauer spectrometer is fairly simple; a scheme is shown in Fig. 25a. A radioactive γ-ray source is attached to a vibration mechanism (drive) that imparts a Doppler shift to the emitted γ-ray energy. The modulated γ-ray passes through the sample where that component with the