

Applications Of Mössbauer Spectroscopy

Mehmet AYDIN

ÖZET

Bu çalışmada, Mössbauer olayı ve Mössbauer parametreleri basit ve öznlü bir şekilde sunulmuştur. Güçlü bir araştırma aracı olan Mössbauer spektroskopisi tekniğinin kullanma yerlerinden örnekler verilmiştir.

ABSTRACT

In this work, the Mössbauer effect and Mössbauer parameters have been briefly discussed. Some applications of the Mössbauer spectroscopy technique as a powerful research tool in various fields has also been shown.

I. INTRODUCTION

The Mössbauer effect is a nuclear physics phenomena discovered by Rudolf L. Mössbauer in 1959. As soon as it was realized that the Mössbauer line is extremely narrow and allows hyperfine interactions to be resolved, it became the basis for a new technique, called Mössbauer or gamma - resonance spectroscopy.

The Mössbauer spectroscopy provides a sensitive and non-destructive method of investigating the interaction of an atom (or, strictly, the nucleus) with its environment. Although many years have passed since the discovery of the effect, the Mössbauer technique is still an up-to-date powerful tool useful in nearly all fields of natural and biological sciences such as solid state physics, chemistry, physical metallurgy, geology, mineralogy, biochemistry, nuclear physics and even archaeology. The technique

(*) Prof. Dr. Ege University, Department of Chemical Engineering.

has already been applied in a wide range of investigations and the number of publications on the subject is still continuous to grow. By using the Mössbauer spectroscopy technique, some fundamental information may be obtained on structures, composition, magnetism and bonding in compounds, alloys and intermetallic phases. The technique has been used to identify, and sometimes to analyse quantitatively, the components of mixtures, mineral ores, etc.

Many articles and books describe the basic aspects of the Mössbauer effect and sophisticated applications of this spectroscopy technique (1, 2, 3, 4).

It is not our purpose here to discuss the physics of Mössbauer effect. An elementary introduction on the effect and technique will be given. Some applications of the Mössbauer spectroscopy technique will then follow. No attempt will be made to discuss any particular topic in detail.

II. THE MÖSSBAUER EFFECT

The Mössbauer effect is the emission and resonant absorption of γ -rays by nuclei bound in solids in which there is no energy loss due to nuclear recoil. The recoil momentum is taken by the crystal as a whole, with negligible energy transfer to or from the lattice vibrations.

The Mössbauer effect is also called «the nuclear resonance fluorescence», and it enables a spectrum to be observed for certain nuclei about 40 elements having excitation energies in the range of 10-100 keV. Fe^{57} and Sn^{119} are two good examples, having nuclear energy states of 14.4 keV and 23.8 keV, respectively. Energy splittings and shifts of the Mössbauer nuclei may be deduced due to their interactions with the electric and magnetic fields of surrounding electrons.

We obtain a Mössbauer spectra with a relatively simple apparatus shown in Fig. 1. The basic equipment consists of a radioactive source, a

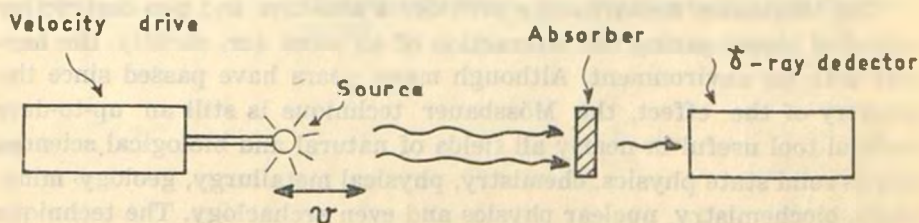


Fig. 1 — Mössbauer effect experiment

resonant absorber and a γ -ray detector. The detector is used to observe the transmitted radiation through the absorber. Here the source is moved back and forth with precisely controlled velocity v to modulate the γ -ray energy by means of the Doppler effect.

A Mössbauer nucleus emits a gamma-ray when it drops from an excited state to the ground state or to a lower state. If this gamma-ray falls on a similar nucleus which is in its ground state, it may be absorbed resonantly and the second nucleus excited. Such resonant absorption depends on an exact match between the nuclear excitation energy and the energy of the incident gamma-ray. However, these energies are not usually the same because the emitting nucleus will recoil. The energy of the gamma-ray is therefore less than the nuclear transition energy.

Let E_0 be the energy of the excited state, M the mass of the emitting nucleus and c the speed of light; then the recoil energy will be $R = E_0^2 / 2Mc^2$. Thus, the energy spectrum of γ -rays emitted from identical nuclei at rest will be centered at energy $E_0 - R$. A γ -ray can be resonantly absorbed by a similar nuclei if, and only if, it possesses an energy of $E_0 + R$. Therefore the spectrum of such γ -rays will be centered at energy $E_0 + R$ shown in Fig.2. For Fe^{57} , the recoil energy of a free atom is 2×10^{-3} eV and

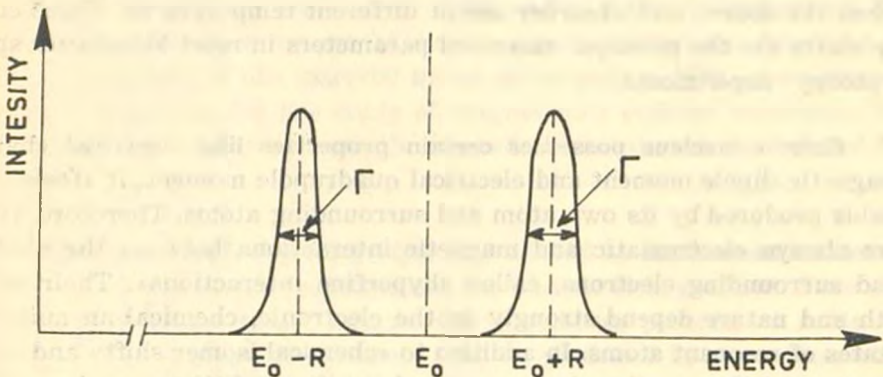


Fig.2 — The effect of recoil on the γ -ray energy spectrum.

the line width is 4.6×10^{-9} eV. Therefore, the resonant absorption and reemission of γ -rays can not occur for free atoms. However, Mössbauer discovered that if, instead of considering γ -ray emission from free atoms, one were to consider the emission of γ -rays from nuclei embedded in a

solid crystal, then the situation would be altered. There will then be a fraction of the nuclei which will emit or absorb gamma rays without any recoil.

The nuclear resonance absorption can be detected in terms of the decreased transmission of γ -rays through the absorber containing the similar nuclei. For maximum absorption, the transmitted intensity is minimum. If the surrounding of emitting and absorbing nuclei are exactly the same, then a maximum resonant absorption occurs at zero Doppler velocity. If the source moves with respect to the absorber, then the overlap of the two lines decreases and less radiation is absorbed. When the relative velocity becomes large enough, the resonant absorption disappears completely.

In practice, the surroundings of emitting and absorbing nuclei are usually different, resulting in small changes in the magnetic and electric fields on the resonant nuclei. Under these circumstances, the resonant absorption occurs at a certain Doppler velocity v_0 and the Mössbauer line will be shifted by an amount $\delta_0 = (v_0/c) E_0$, called the «chemical isomer shift» or just «isomer shift».

Another important energy shift is the «temperature shift». It occurs when the source and absorber are at different temperatures. These energy shifts are the principal measured parameters in most Mössbauer spectroscopy experiments.

Since a nucleus possesses certain properties like electrical charge, magnetic dipole moment and electrical quadrupole moment, it «feels» the fields produced by its own atom and surrounding atoms. Therefore, there are always electrostatic and magnetic interactions between the nucleus and surrounding electrons, called «hyperfine interactions». Their strength and nature depend strongly on the electronic, chemical and magnetic states of resonant atoms. In addition to «chemical isomer shift» and «temperature shift» mentioned above, the «hyperfine splittings» and «quadrupole splittings» of the Mössbauer line tend to be different for different solid surroundings. Thus, measurements of all these parameters are the primary results in most Mössbauer experiments.

III. MÖSSBAUER PARAMETERS

The major parameters used in Mössbauer studies and derived from Mössbauer spectra are the following: the isomer shift, the temperature

shift, the hyperfine magnetic splitting, the quadrupole splitting and the recoil - free fraction (called Debye - Waller factor).

The isomer shift (IS) is the difference between the nuclear transition energies of the absorber and the source. It arises from the fact that the nucleus is not a point source, but interacts as a region of spherically symmetrical charge space with the surrounding electronic charges, which are s - electrons. Changes in the s - electron population affect the isomer shift directly and variations in the number of p - or d - electrons have an indirect shielding effect. It is normally possible to use the measured IS to determine the electronic density at the resonant nucleus, which has an immediate application to chemical bonding. It usually provides enough information to determine the valence state of the ion.

The isomer shift is just a Doppler energy shift of the Mössbauer line, so it does not split the energy levels. However, the hyperfine interaction (HFS) splits the nuclear energy level without changing the center of gravity of the spectrum. The strength and sometimes the direction of the magnetic field at the nucleus may be determined by using HFS. In ferromagnetic, antiferromagnetic, and some paramagnetic materials, the magnitude of the magnetic field can be related to various mechanisms for the coupling of electronic and nuclear spins, and to relaxation processes. Thus, the HFS measurements can be used to draw conclusions about the electronic structure of the material under investigation. HFS interaction provides a technique for the study of magnetically ordered materials; Curie or Néel temperature and atomic magnetic moments can be deduced from it.

The quadrupole splitting (QS) is produced by the interaction between the nuclear quadrupole moment and the electric field gradient. Pure α - Fe does not give this effect because the iron lattice possesses a cubic symmetry. The electric field gradient may be produced by a nonsymmetrical (non - cubic) arrangement of the ions surrounding the Mössbauer atom. It may also arise from a nonsymmetrical distribution of the electrons of the Mössbauer atom as in high - spin ferrous and low - spin ferric complexes. The QS is also produced when the other atoms bound to the Mössbauer atom are not identical or are arranged nonsymmetrically. Thus, the QS is very sensitive to the structure of the system and to the differences in bonding between the Mössbauer atom and its immediate neighbours. In analytical applications, the measured isomer shift, hyperfine magnetic sp-

litting, and quadrupole splitting can be compared with those of known compounds to identify the phases and the material being studied.

The Debye - Waller factor (f) is a measure of the tightness of binding of the Mössbauer atom in its lattice. From the value of f , the Debye temperature and mean square displacement of the Mössbauer atom can be determined.

IV. APPLICATIONS

The Mössbauer spectroscopy technique is very well suited to the qualitative and quantitative analysis of many substances. The accuracy in quantitative estimations is about 2 - 5%. Numerous applications can be found in all natural and biological sciences. We intend to mention only a few of them, demonstrating the range of problems considered and the types of results obtained.

a) Solid State Physics

The Mössbauer technique has been widely used in solid state physics, particularly in the study of magnetic materials. One of the earliest applications was the determination of the magnitude and sign of the effective magnetic field on Fe^{57} nuclei in α -Fe (5,6). Since then, numerous measurements have been made on magnetically ordered salts, garnets, alloys and intermetallic compounds using a Co^{57} source (7). The effect of the core polarization and the conduction electron polarization on the value of the effective magnetic field on resonant nuclei has been studied (8). For dilute alloys of non - magnetic atoms in iron, the variation in conduction electron polarization depending on the distance from an impurity atom has been investigated (9). f -factor measurements have given valuable information about the dynamics of solids and liquids (10).

b) Physical Metallurgy

Iron is the most important element in metallurgy. An alloy containing some amount of iron is either a single phase or a multi - phase alloy. In steels, for example, austenite, ferrite, martensite, cementite and ϵ -carbide are the main phases.

A Mössbauer spectrum can be broken down into its components to obtain information about individual phases in the absorber. Therefore, problems in order - disorder alloys, interstitial alloys, solid solution alloys,

ferromagnetic alloys, precipitation, diffusion, oxidation and lattice defects etc, can be investigated using the Mössbauer technique.

In plain carbon steels, ferrite and martensite are ferromagnetic phases giving rise to a six - line spectrum, while austenite is a paramagnetic phase and gives a single line. Marcus et al. (11) and Crist and Giles (12) have used this fact to determine the amount of retained austenite in steels.

Precipitation, phase determination and oxidation processes in Cu-rich Cu - Fe alloys under different annealing and quenching conditions have been studied in detail (13, 14, 15, 16). Mössbauer studies on iron - nickel alloys (17), and iron meteorites (18) have led to the discovery of the existence of a 50% - 50% Fe - Ni phase, called «ordered phase» or «superstructure», in kamacite lamellae of Cape York iron meteorite.

c) Chemistry

The Mössbauer spectroscopy technique has already been applied to many kinds of chemical problems. It has become customary to attempt to correlate chemical properties with data on the isomer shift and quadrupole splitting. In the field of structural chemistry, the procedure has particularly been used in studying iron and tin compounds to determine the structure of valence electron shells of the Mössbauer atoms and bond properties, e.g. σ - and π - interaction between the Mössbauer atom and bonded ligands. The technique has also been found to be a powerful tool in identifying chemical species qualitatively and quantitatively.

In tin chemistry, Mössbauer spectrometry has been used to confirm that compounds of the type R_4Sn contain quadrivalent tin for which a QS is normally observed only for organo metallic compounds. While the QS value is partially dependent on the nature of the substituents, it is much more dependent on the structure of tin. Thus, compounds of the type R_3SnX have QS of 1.0-2.2 mm/sec if monomeric or 3.0-3.5 mm/sec if polymeric. On this basis it appears that many halides (19) and carboxylates (20) are polymeric, but carboxylates in the solid state to be monomeric.

d) Biochemistry

The Mössbauer spectrometry is quite useful as a quantitative and qualitative analytical tool in research and in more detailed studies of the state of iron in biological molecules. Using this technique, several systems, mainly iron - containing proteins, have already been examined.

In Johnson's work (21), it has been shown that the Mössbauer spectra of lung material from a normal person and from a victim of hemosis-derosis are quite different. The spectrum of the diseased lung indicates abnormally large amounts of iron in the form of a finely divided, low molecular weight compound.

Mössbauer studies on hemoglobin complexes have shown that the Mössbauer parameters are very dependent on the nature of the sixth ligand (O_2 , N_2 , CO , F^- , CO) (22).

Acknowledgements. I am grateful to Miss Nihâl Göğeren for the typing of the manuscript and to Dr. and Mrs. Turgay Ertürk for the kind help to use better English in writing the article.

REFERENCES

- (1) Fraunfelder, H., *The Mössbauer Effect*, Benjamin, New York, 1962.
- (2) Aydın, M., *COMMUNICATIONS*, Teme 22 A, 67 (1973)
- (3) Goldenskil, V.J. and Herber, R.H. (ed.), *Chemical Applications of Mössbauer Spectroscopy*, Academic Press, New York, 1968.
- (4) Greenwood, N.N. and Gibb, T.C., *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971.
- (5) Hanna, S.S., Heberle, J., Littlejohn, G., Perlow, G.J., Preston, R.S., and Vincent, D.H., *Phys. Rev. Letters*, 4, 177 (1960)
- (6) Preston, R.S., Hanna, S.S., and Haberle, J., *Phys. Rev.*, 128, 2207 (1962).
- (7) Danon, J., in Goldenskil and Herber (3).
- (8) Hufner, S. and Wernick, J.H., *Phys. Rev.* 173, 448 (1968).
- (9) Stearns, N.B., *Phys. Rev.* 147, 439 (1966).
- (10) Boldenskil, V.I. and Markarov, E.F., in Goldenskil and Herber (3).
- (11) Marcus, H., Schwartz, L.H., and Fine, M.E., *Trans. ASM*, 59, 468 (1966).
- (13) Gonser, U., Grant, R.W., Muir, A.H., and Wiedersich, H., *J. Appl. Phys.*, 36, 2124 (1965).
- (14) Aydın, M., *METU J. of Pure and Applied Sciences*, 7, 113 (1974).
- (15) Window, B., *J. Phys. C: Solid State Phys.*, 3, 922 (1970).
- (16) Aydın, M., *METU J. of Pure Applied Sciences*, 8, 373 (1975)
- (17) Paulevč, J., Dautreppe, D., *Compt. Rend.*, 250, 3804 (1960).
- (18) Petersen, J.F., Aydın, M. and Knudsen, J.M., *Phys. Letters*, 62A, 192 (1977).
- (19) Gasseheimer, B. and Herber, R.H., *Inorg. Chem.*, 8, 1120 (1969).
- (20) Ford, B.F.E., Liengme, B.V. and Sams, J.R., *J. Organomet. Chem*, 19, 53 (1969).
- (21) Johnson, C.E., *Physics Today*, 24, 35 (1971).
- (22) Gonser, U. and Grant, R.W., *Biophys. J.*, 5, 823 (1965).