PROGRESS IN MÖSSBAUER SPECTROSCOPY

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(Receiveed November 1989)

ABSTRACT

Mössbauer effect, a nuclear analogue of resonance fluorescence, has proven to be one of the most effective experimental methods for the scientific investigation in a large variety of problems from nuclear physics to medicine. The popularity of the method is due to the fact that it allows one to carry out experiments with the highest energy resolution. Approximately 1000 articles have been published during each of the last 10 years. In this review, we will discuss some of recent developments in this field, the applications in natural science, and some industrial applications. Finally, the general conditions of Mössbauer spectroscopy will be discussed and the present situation of this field in China will be involved.

Key words: Mössbauer spectroscopy

More than 30 years ago, R.L.Mössbauer pointed out that the emission and absorption of gamma-rays could occur in a recoil-free mode.

This discovery has developed into the well established powerful and versatile method, known as Mössbauer spectroscopy, for a large variety of branches of the natural sciences from nuclear physics to medicine.

Mössbauer spectroscopy is still very much alive at present and continues to delight us with elegant solutions to old problems, unanticipated glimpses at new phenomena, clever uses of new technical possibilities, and ingenious applications to fields far away from physics[1].

Mössbauer effect has many unique features that make this method of special interest for scientific studies. The chief attraction of the Mössbauer effect is the highest energy resolution ($\Delta E/E \sim 10^{-13}$ for ^{57}Fe) under the condition of using relatively simple experimental apparatus. For example, in the resolution in measuring the distance between the earth and the moon, $\Delta L/L \sim 10^{-13}$ implies that it is measured by $\sim 10^{-3}$mm. We can say that the popularity of the method is due to the fact that it has the highest energy resolution in all physical skills. Since this discovery, the energy detectability for gamma-ray has been raised to more than eight orders from 0.1 eV. One of the earliest and most striking applications was the confirmation of the effect of gravity on photon energy predicted by Einstein.

The extreme narrowness of the resonance spectrum allows us to measure the small perturbations (10^{-6}—10^{-10} eV, typically) of the nuclear levels produced by the hyperfine interactions between the nucleus and its surroundings. Such hyperfine interactions are very important because of the information they provide deals with the microscopic structures of the materials. This is another reason for its popularity.

In this paper we will discuss some of the most recent developments in this fiels.

I. NEW DEVELOPMENTS IN MÖSSBAUER EFFECT METHODOLOGY

The observations of five new Mössbauer transitions have been reported since 1980. Therefore, Mössbauer resonance has been observed in 46 elements, 92 isotopes and 112 excited states.

The special Mössbauer isotopes, ^{67}Zn (▲ $E/E \sim 5.3 \times 10^{-16}$), ^{181}Ta (▲ $E/E \sim 10^{-14}$) and ^{73}Ge (▲ $E/E \sim 9 \times 10^{-14}$) have attracted much attention for their extremely high energy resolution.

Synchrotron radiation offers a new type Mössbauer source and has unique features (brilliance, time structure, polarization, collimation, ...) in comparison with the radioactive source. Alternatively, synchrotron radiation which has been resonantly filtered by means of the Mössbauer effect, offers a new X−ray source for the X−ray optics with 10^{-6}eV resolution. Time differential measurements have the potential to improve greatly the accuracy of future experiments[2].

High sensitivity and depth selectivity are the essential features of conversion electron Mössbauer spectroscopy (CEMS). In the past few years, CEMS has grown rapidly as a new tool of surface investigation[3]. A major development is the use of this technique at low temperatures. Now it can be used as low as 4.2 K. Microfoil Internal Conversion Electron (MICE) detector gives a large improvement in the ratio of signal to noise for many Mössbauer isotopes when compared to the transmission mode.

The studeis of coherent phenomena in Mössbauer resonant diffraction have been developed lately[4]. The recent success in filtering Mössbauer quanta out of the synchrotron radiation and in diffraction observation of the synchrotron radiation from a Mössbauer nuclei marked the begining of a new stage.

In the past few years an increasing attention has been devoted to the Rayleigh scattering of Mössbauer radiation (RSMR), it seems to be very effective in the studies of atomic and molecular dynamics, especially in the slow motions in macromolecular systems. It combines the advantage of both methods: Rayleigh scattering contains information on all atoms of the sample while the use of Fe Mössbauer radiation sets a time threshold of 10^{-7} s[5]. The dynamics of myoglobin has been studied by means of RSMR[6]. The results show that the wet myoglobin molecular segments move collectively with $\langle X^2 \rangle = 0.0027$ (nm)^2, and freeze dried myoglobin with $\langle X^2 \rangle = 0.0006$(nm)^2 just as normal solid state vibrations. This is a new information in biochemistry.

In Mössbauer polarimetry the source and the absorber take the place of the polarizer and analyzer used in optical polarimetry. The use of polarized resonance gamma-ray includes observing Mössbauer-Faraday effect and "optical" rotation, establishing the gamma-ray rotation polarimetric method, determining the magnitude and the direction of the hyperfine field vectors[7].

The effect of the radiofrequency modulation of the Mössbauer gamma radiation (radiofrequency sidebands) and that of the fast relaxation of the magnetic hyperfine field induced by the radiofrequency field (radiofrequency collapse) gaim much attention lately. Radiofrequency collapse of the magnetic splitting allows direct determination of the quadrupole splitting in ferromagnetic amorphous metals providing the method for studying the short range order. The effect of radiofrequency induces crystallization of amorphous metals and its relation to radiofrequency sidebands has also been confirmed[8].

The idea of Mössbauer imaging has been proposed by S. J. Norton in 1987[9]. A conventional Mössbauer experiment measures only a bulk average of Mössbauer parameters inside the absorber. The aim of Mössbauer imaging is to reconstruct and display its spatial distrubution, i.e., to do spectroscopy as a function of position inside a sample, rather than in bulk. In Mössbauer imaging, a velocity gradient is imposed along the radial direction of the absorber and the resonance associated with a particular Doppler shift takes place along a family of lines perpendicular to the velocity gradient. It is analogous to the NMR magnetic field gradient in NMR imaging. Spatial resolution is proportional to the ratio of the natural linewidth to the rotational velocity of the absorber. Some potential applications in material science include the analysis of heterogeneous materials, the imaging of grain boundary segregation, the imaging of residual stress distribution and the distribution of magnetism in ferromagnetic materials.

II .THE ACTIVITIES IN A LARGE VARIETY OF BRANCHES OF THE NATURAL SCIENCES

Mössbauer spectroscopy has now reached the age of maturity and it has been providing a wealth of information for a large variety of fields in natural sciences. We will furnish the following examples.

Mössbauer spectroscopy is an important tool in solid state physics and physical metallurgy. It is a microscopic probe that measures local properties of certain atoms incorporated in a solid via hyperfine interactions. With its high resolution, it provides valuable information regarding a broad topics, such as phases, states, defects, surface phenomena, film behaviour, order-disorder phenomena, texture, magnetic properties, lattic dynamics, etc.

In recent years amorphous materials have received considerable attention from physical point of view and also because of their technological importance. The Mössbauer spectroscopy has been making important contribution to the study of amorphous materials. It reveals the atomic scale structure of these materials by correlating the distributions of the Mössbauer parameters with appropriate models. Mössbauer spectroscopy can also be used to study the stability of the amorphous materials, the surface crystallize, and other properties.

The combination of ion implantation and Mössbauer spectroscopy has developed into a very important field. Mössbauer spectroscopy is a fruitful tool to study the neighbourhood of the implanted atoms and the implantation process itself, to determine the submicroscopic structure and the sites of impurities, to understand the structural properties and electronic properties of the system[10]. Many of the studies on ion implantation involve the use of CEMS, which is an excellent tool because it is surface-sensitive.

The study of synthetic metals including the organic superconductors, the transition metal dichalcogenides and one-dimensional system with spin and charge density waves, is a very active field in recent years. Mössbauer spectroscopy provides a sensitive means for the identification of the chemical forms, the structural properties and the bonding strength of the intercalated or inserted species, and for the elucidation of charge transfer in many synthetic metal systems[11].

Mössbauer spectroscopy has established itself as a valuable method in the studies of high-Tc superconductors. It is important in showing that Mössbauer effect contributes to this rapidly expanding field. The cuprate perovskites with compositions $RBa_2Cu_3O_7$, where R includes most of the rare earths, are particularly interesting. ^{57}Fe Mössbauer spectra for Fe-doped $RBa_2Cu_3O_7$ superconductor have been used to determine unambiguously the oxidation state of the substituted Fe ions as well as their enviroment. The results show that Fe cations are substituted for both Cu(1) and Cu(2) sites, but the substitution is preferentially taking place on Cu(1) chain sites at $x<3\%$. The Fe cations at Cu(1) chain sites exhibit anisotropic vibration. Three different types of oxygen coordinations of Fe(1) cations are identified by the point change model. The calculations indicate that Fe^{3+} are present in tetrahedral, pyramidal, and distorted octahedral coordinations, as well as Fe^{4+} in pyramidal and distorted octahedral at Cu(1) sites[12]. The results also show that the behavior of these materials with respect to the magnetic impurity differs from that of the conventional BCS-type superconductors. The iron cations induced a structural transition from orthorhombic to tetragonal with increasing iron contents. However, Tc was almost unaffected by the substitution up to 4%[13]. There is a softening in vibrational modes localized onto the Cu-O linear chains at $T<110K$[16]. On the other hand, through

Mössbauer study of structure and magnetic ordering of $GdBa_2(Cu_{0.94}Fe_{0.06})_3O_7$ superconductor, the coexistence of superconductivity and magnetic order have been observed at 4.2K. It implies that both the magnetic ordering and the superconductivity seem to involve the Cu - O layers[16].

Mössbauer spectroscopy has attractive applications in the study of biological systems. The theoretical and practical problems concerned in this area might be more than those in others. Many biological molecules contains iron at their active centers, therefore Mössbauer effect can be used as a powerful local probe for the chemical state of iron as well as their environments, and it can provide some information which could not be obtained by any other method. A major contribution is the determination of the iron electronic states in many proteins, such as haemoproteins, iron sulphur proteins, iron storage and transport proteins[17]. In addition, a number of investigations of dynamics of iron atoms within protein molecules have been made by using Mössbauer spectroscopy. Recently a solution of the phase problem in the structure determination of biological macromolecules by using the nuclear resonance scattering on an Fe nucleus as reference has been suggested[1].

It should also be noted that the possibility of creating a gamma - ray laser (GRASER) based on the use of isomeric nuclear transitions and the use of pulsed pumping of gamma laser has been discussed ever since 1963. The minimum requirements for superradient gamma - ray emission has been given[18] and found that if a pure sample of a storage isomer can be rapidly transferred into an inverted population for a recoilless transition, less than 10^{13} nuclei should be sufficient for an experimental demostration of nuclear superradiance.

Ⅲ. INDUSTRIAL APPLICATIONS OF MÖSSBAUER SPECTROSCOPY

The oldest and maturest technological applications is that in iron and steel industries. Its history lasts for more than 15 years. In table 1[19] we see that Mössbauer spectroscopy is being utilized in broad aspects of the steel industry.

The Mössbauer effect has also found its use in coal, minerals and mineral processing. It can be used effectively to monitor the pyrite and other iron sulphides through various coal treatment processes, including coking, sulphur removal, liquefaction and gasification.

Another active area for Mössbauer spectroscopy related to industrial application is the study of catalysts. Mössbauer spectroscopy is one of the few techniques that allows ultra high - vacuum surface science studies, as well as in situ studies of catalysts under conditions typical of the catalytic reaction, so it has become a very important means for studying many catalyst systems. The technique may provide unique information about many problems such as: (1) the nature and concentration of the phases present in the working state of a catalyst (also in the case where the catalysts contain multiphasic, microcrystalline or amorphous structures), (2) support interactions, (3) preparation, activation and deactivation phenomena, (4) particle size, (5) surface structure and composition, and (6) active sites[20].

Table 1

Mössbauer spectroscopy in steel industry[19]

Steel making process	Steel surface process	Steel corrosion studies	Metallurgical studies
Ore selection and analysis	Nitrided surface	Bulk corrosion surface corrosion	Composition phase transformation
Sinter monitoring	Carbided surface	Protective layers	Retained austenite
Direct ore reducation	Borided surface	Corrosion products	In ferritic steels
Coal characterization	Galvanized surface	Corrosion process	Ferrite in austenitic welds and castings
Monitoring of pyrite content	Aluminized surface	Inhibitor influence	Precipitation hardening
Boiler ash and Slag Studies	Coated Steels	Ion implanted surfaces	Wear– resistance
End product Phase analysis	Wear and hardness Implanted steels Case hardened Surface stresses	Alloyed surfaces	Tempering cold Aging Heat treatment

A general overview of the important areas which are directly or indirectly related to the industrial applications is shown in Table 2[21].

Table 2

Industrial areas of application of the Mössbauer effect[21]

Classical applications	Steel industry, coke, coal, mining industry (minerals), special alloys
Amorphous system	Metallic, semiconductors, insulators
Interfaces & surfaces	Semiconductor/metal, composite materials, multilayers system, Surface properties (corrosion, etc.)
Magneting recording	
Biotechnology	
Energy technologies	Solar energy, fuel cells, petroleum processing, synthetic fuels, coal, sheales, tar sands etc. radioactive waste management

Now let us turn back to discuss the general situation of the Mössbauer spectroscopy research.

During the last ten years, the interest in Mössbauer spectroscopy has continued at high level, approximately 1000 articles (not including conference proceedings) per year were published each year.

We might observe the following trends in the developments of Mössbauer spectroscopy:

(1) The analysis becomes more quantitative rather than qualitative.

(2) The experimental method becomes more sophistical rather than "classical".

(3) The investigated samples are not only crystalline, but also noncrystalline.

(4) The use of Mössbauer spectroscopy is not within the limits of fundamental research, more and more industrial applications can be seen.

During past decade, the interest in Mössbauer spectroscopy is decreasing slightly in the developed countries, while at the same time there is an impressive increase in the developing countries, primarily China and India. In August 1986, the South – North Roundtable on Mössbauer spectroscopy was held in Trieste by the Third World Academy of Sciences. In the final report of that meeting, the situation of Mössbauer spectroscopy in the developing countries was demostrated as follows: "Mössbauer spectroscopy can be used in any Third World lab and therefore it can promote transfer of technology effectively in the Third World. Research and applications can be carried out without having necessarily the need for sophisticated labs. The technical applications can be of particular interest for the Third World countries, for example, the investigation of minerals, coals, soils studies, environmental problems, corrosion and catalysis. The number of application is continuously increasing and involves all domains including life and technology".

Mössbauer spectroscopy in China is in a period of rapid development. At present there are about one hundred Mössbauer research groups spreading all over China. About 300 Chinese scientists are engaged mainly in the applications of Mössbauer spectroscopy to the various fields. About 120 papers per year were published in China on Mössbauer spectroscopy in the past few years. In the concluding remarks for the International Conference on the Applications of the Mössbauer Effect in 1987, it was pointed out that China in particular has made a great leap into Mössbauer activities. For example, such activity in China are more than that in France and England. It has been decided that the International Conference on the Applications of the Mössbauer Effect in 1991 will be held in Nanjing, China.

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