

Mössbauer Effect

Current Applications to Physical Sciences

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MÖSSBAUER EFFECT
CURRENT APPLICATIONS TO PHYSICAL SCIENCES

Preface

The discovery of observing recoilless emission and absorption of gamma rays by Professor Rudolf L. Mössbauer in 1957 has been one of the most important discoveries in recent years. It laid the foundation of a new spectroscopic technique with extremely high resolution. Soon after this discovery, it was realised that Mössbauer Effect will have extensive bearings on many different disciplines of modern science. It is now being extensively used to study diverse problems in physical, chemical, biological and metallurgical sciences. Sophisticated equipment for Mössbauer studies is now commercially available and this has given a big boost to research activities in Mössbauer spectroscopy all over the world.

In India, research on Mössbauer Effect is being carried out in about thirty universities and several scientific research institutes. Because of this large interest in the field, an International Conference on Applications of Mössbauer Effect was held at Jaipur, India, in December 1981. In order to avail of the opportunity of the visit of experts in different aspects of Mössbauer Spectroscopy, Dr. V.G. Bhide, Chairman of the Organising Committee of the International Conference, suggested that we organise a **Workshop on the Applications of Mossbauer Effect** at the University of Delhi just before the International Conference. Thus, the University of Delhi hosted this Workshop at the Department of Physics and Astrophysics from 2-11 December 1981 through an Organising Committee comprising of Professor L.S. Kothari (Director), Professor J.S. Bajjal (Convenor), Professor G.P. Srivastava, Dr. V.G. Bhide and Dr. S.P. Tewari. The Workshop was attended by about eighty physicists, chemists and geologists from India and abroad. Several internationally known specialists in Mössbauer Spectroscopy accepted the invitation of the Organising Committee to deliver lectures at the Workshop. These were Dr. V.G. Bhide (India), Professor J. Chappert (France), Professor Richard L. Cohen (USA), Dr. S. Dattagupta (India), Professor P.A. Montano (USA), Professor James G. Mullen (USA), Professor R.V. Parish (UK), Professor J.G. Stevens (USA) and Professor T. Zemcik (Czechoslovakia).

The present book is essentially based on the material presented at the Workshop. It is a collection of the articles based on lectures delivered by some of the distinguished guests. We have also included contributions from those who could not be present due to various reasons but have sent their contributions for inclusion in this book. The different chapters in the book are self-contained and cover different applications of Mössbauer Effect. The

notation used by different authors is not always uniform, but we have kept the same notation as used by the authors.

The book opens with the Nobel Lecture of Professor Rudolf L. Mössbauer which provides an excellent and befitting introduction to this exciting field of Mössbauer Spectroscopy. Professor Mössbauer's other paper 'Random Atomic Motion in Proteins' is appearing for the first time in English. (It has earlier appeared in the Russian language.) Among the other topics covered in this volume are the study of diffusive motions using a newly developed MICE detector; relaxation effects; applications to materials science research; molecular solids, polymers and microcrystallites; use of hydrogen-storage materials in energy devices. It also contains other topics describing the use of Mössbauer spectroscopy in studying magnetic properties of amorphous alloys, thin film phenomena and problems of interest in chemical science. In the end some work on Mössbauer instrumentation, such as the design of a servo system for Mössbauer spectrometer and its use for difficult isotopes has also been included.

Acknowledgments

We would like to express our sincere thanks to Professor Rudolf L. Mössbauer, the Nobel Foundation and the Editors of *Science* for permission to publish the Nobel Lecture. We are also grateful to Professor Mössbauer for sending us his second paper on 'Random Atomic Motions in Proteins' for publication in this book. We would also like to acknowledge with thanks the permission granted by the Editors of *Science* to reprint the paper 'Hydrogen-Storage Materials: Properties and Possibilities' by Richard L. Cohen and J.H. Wernick; *Chemical Physics Letters* to reprint the paper 'Mössbauer Spectroscopy of Frozen Solutions' by Richard L. Cohen and K.W. West; and *Journal de Physique (Paris)* to reprint the paper 'Mössbauer Studies of Hydrogen-Absorbing Rare-Earth Intermetallics' by Richard L. Cohen. We would like to thank Professor Gurbakhsh Singh, Vice Chancellor, University of Delhi and Professor D.S. Kothari, Chancellor, Jawaharlal Nehru University, for their guidance and help.

We would like to record our thanks and appreciation for the generous help of University Grants Commission, Department of Science and Technology, Government of India and Indian National Science Academy. We would also like to thank our colleagues in the Department of Physics and Astrophysics and the many research students who helped us in the successful organisation of the Workshop.

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Workshop on Mössbauer Effect and its Applications

Department of Physics and Astrophysics, University of Delhi
2-11 December 1981

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MÖSSBAUER EFFECT:
CURRENT APPLICATIONS TO PHYSICAL SCIENCES
L.S. Kothari, J.S. Baijal and S.P. Tewari (editors)
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Recoilless Nuclear Resonance Absorption of Gamma Radiation

Rudolf L. Mössbauer

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It is a high distinction to be permitted to address you on the subject of recoilless nuclear resonance absorption of gamma radiation. The methods used in this special branch of experimental physics have recently found acceptance in many areas of science. I take the liberty to confine myself essentially to the work which I was able to carry out in the years 1955 to 1958 at the Max Planck Institute in Heidelberg, and which finally led to establishment of the field of recoilless nuclear resonance absorption. Many investigators shared in the preparations of the basis for the research we are concerned with in this lecture. As early as the middle of the last century Stokes observed, in the case of fluorite, the phenomenon now known as fluorescence—namely, that solids, liquids, and gases under certain conditions partially absorb incident electromagnetic radiation which immediately is re-radiated. A special case is the so-called resonance fluorescence, a phenomenon in which the re-emitted and the incident radiation both are of the same wavelength. The resonance fluorescence of the yellow D lines of sodium in sodium vapour is a particularly notable and exhaustively studied example. In this optical type of resonance fluorescence, light sources are used in which the atoms undergo transitions from excited states to their ground states (Fig. 1). The light quanta emitted in these transitions ($A \rightarrow B$) are used to initiate the inverse process of resonance absorption in the atoms of an absorber which are identical with the radiating atoms. The atoms of the absorber undergo a transition here from the ground state (B) to the excited state (A), from which they again return to the ground state, after a certain time delay, by emission of fluorescent light.

This article is the English version of the lecture which the author delivered at Stockholm, Sweden on 11 December 1961, when he received the Nobel Prize in Physics. Permission to re-publish the article [*Science* 137, 731-38 (1962)] granted by the Nobel Foundation, is gratefully acknowledged.

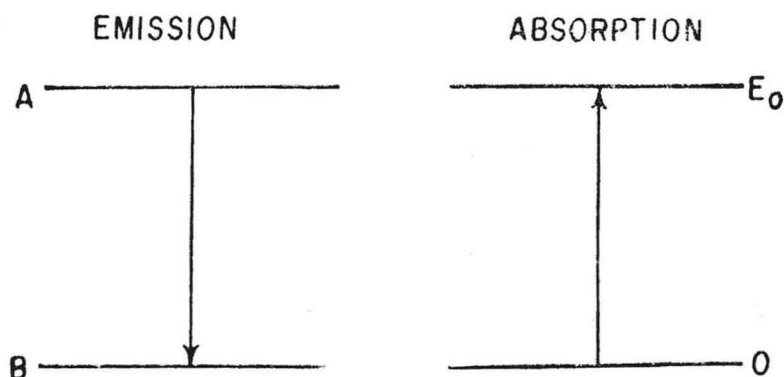


Fig. 1. Scheme of resonance absorption.

As early as 1929, Kuhn [1] had expressed the opinion that the resonance absorption of gamma rays should constitute the nuclear physics analogue to this optical resonance fluorescence. Here, a radioactive source should replace the optical light sources. The gamma rays emitted by this source should be able to initiate the inverse process of nuclear resonance absorption in an absorber composed of nuclei of the same type as those decaying in the source. Again, the scheme of Fig. 1 would hold here, but the radiative transitions would now take place between nuclear states. Nevertheless, all attempts in the next two decades to find this nuclear resonance absorption proved fruitless. Before I can approach the subject of my talk, it is appropriate to consider the reasons why the discovery of nuclear resonance absorption was so long delayed.

For simplicity, we shall first consider a nuclear transition of a free nucleus at rest. The gamma quantum emitted in the transition $A \rightarrow B$ imparts a recoil momentum \mathbf{p} to the emitting nucleus, and consequently a kinetic energy ΔE , which is given by

$$\Delta E = \mathbf{p}^2/2M = E_0^2/2Mc^2 \quad (1)$$

where M is the mass of the nucleus and c is the velocity of light. The energy liberated in this nuclear transition is divided, in accordance with the law of conservation of momentum, the larger part being carried away by the emitted quantum, the other part going to the emitting nucleus in the form of recoil energy. This recoil-energy loss of the quantum has the consequence that the emission line does not appear at the position of the transition energy E_0 but is displaced to lower energy by an amount ΔE (Fig. 2). The absorption line, on the contrary, is displaced to a higher energy by the same amount ΔE , because in order for the process of resonance to occur, a quantum must provide, in addition to the transition energy E_0 , the amount of energy ΔE which is taken up by the absorbing nucleus in the form of a recoil kinetic energy. Typical values for the line shifts ΔE lie in the range from 10^{-2} eV to

10^2 eV; they are, therefore, very small in comparison with the energies of the gamma quanta, which frequently are of the order of magnitude of millions of electron volts.

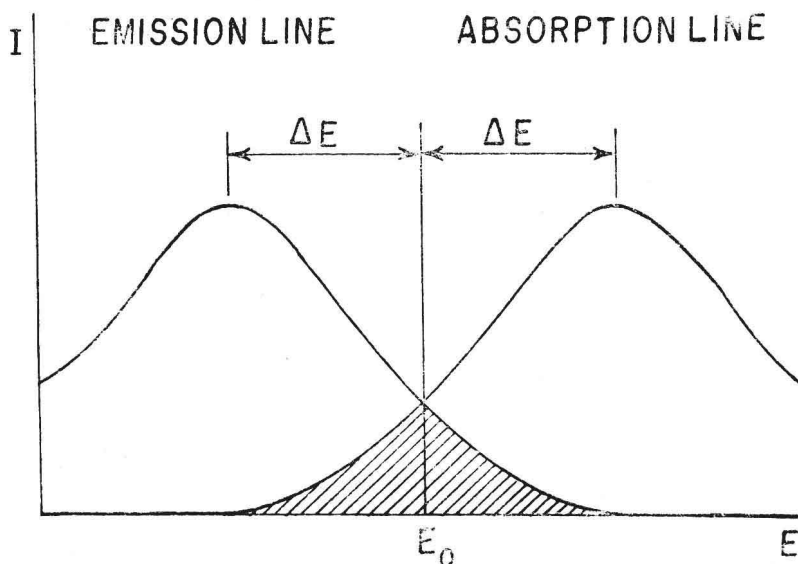


Fig. 2. Position and shape of the emission and absorption lines of a free nucleus (shown in the case of the 129-keV transition in Ir^{191} for $T = 300^\circ\text{K}$).

Since there is an uncertainty in the energies of the individual excited states of the nuclei, the lines associated with transitions between an excited state and the ground state have a certain minimum width. This so-called natural width Γ is, according to the Heisenberg uncertainty principle, connected with the lifetime τ of an excited nuclear state by the relation $\Gamma\tau = \hbar$. The usual values for the lifetimes τ of the low-lying excited nuclear states lie in the range from 10^{-7} to 10^{-11} second, corresponding to an interval of 10^{-8} to 10^{-4} eV for the natural line widths appearing in ground-state transitions. Such extraordinarily sharp lines exhibiting the natural line width are normally not observed. Rather, a series of side effects always exist, which lead to considerable broadening such that the line widths ordinarily associated with low-energy gamma transitions exceed the natural minimum width by many orders of magnitude. The most important broadening mechanism is the thermal motion of the nuclei in the source and in the absorber; this leads to Doppler shifts in the energy of the gamma quanta and therefore produces corresponding line broadenings. Even a temperature drop to absolute zero does not extinguish this thermal broadening, since the existence of zero-point energy at absolute zero frequently produces, at least in solids, line widths of the same order of magnitude as the ones existing at room temperature.

Usually the line shifts ΔE are large in comparison to the thermal line widths, and they are also always very large in comparison to the natural line

widths associated with the low-energy nuclear transitions we are concerned with here. As a consequence, the energy of an emitted quantum is usually too small for the inverse process of resonance absorption to be carried out, or in other words, the probability of occurrence of nuclear resonance absorption is so small that the process escapes detection. Therefore, the long and unsuccessful search for nuclear resonance absorption is to be blamed on the high recoil-energy losses of the gamma quanta.

On the other hand, entirely different conditions hold for optical resonance absorption. There, because of the much lower energies of the light quanta, the recoil-energy losses produced by light quanta are small in comparison with the line widths. Emission and absorption lines, therefore, overlap in an ideal manner, the resonance condition is satisfied, and the optical effect is, at least in principle, easily observable.

The unsatisfactory situation with respect to nuclear resonance absorption first changed in 1951, when Moon [2] succeeded in demonstrating the effect for the first time, by an ingenious experiment. The fundamental idea of his experiment was that of compensating for the recoil-energy losses of the gamma quanta: the radioactive source used in the experiment was moved at a suitably high velocity toward the absorber or scatterer. The displacement of the emission line toward higher energies achieved in this way through the Doppler effect produced a measurable nuclear fluorescence effect.

After the existence of nuclear resonance fluorescence had been experimentally proved, a number of methods were developed which made it possible to observe nuclear resonance absorption in various nuclei. In all these methods for achieving measurable nuclear resonance effects the recoil-energy loss associated with gamma emission or absorption was compensated for in one way or another by the Doppler effect.

Observation of an "Anomalous" Effect at Heidelberg

At this point, let me speak of my esteemed teacher, Heinz Maier-Leibnitz, who in 1953 directed my attention to this newly advancing field of nuclear resonance fluorescence, and who stimulated me to turn to this area of research. He was, also, the one who made it possible for me to conduct my research throughout the years 1955 to 1958 at the Heidelberg Max Planck Institute, in an undisturbed and fruitful atmosphere—research which finally led to the discovery of recoilless nuclear resonance absorption. I want to express my warmest thanks to my esteemed teacher for his efforts on my behalf.

The method which I shall now proceed to discuss differs fundamentally from methods described above in that it attacks the problem of recoil-energy loss at its root in a manner which, in general, insures the complete elimination of this energy loss. The basic feature of this method is that the nuclei in the source and absorber are bound in crystals. The experiments described in

the following paragraphs exclusively employed radioactive sources which emitted the 129-keV gamma line leading to the ground state in Ir^{191} .

The first experiment [3] aimed at measuring the lifetime of the 129-keV state in Ir^{191} by utilizing methods of nuclear resonance absorption known at that time. The experimental setup used for this purpose is shown schematically in Fig. 3. A method first employed by Malmfors [4] appeared to be especially suitable for the planned measurement. In this method, a broadening of the emission or absorption line, leading to a corresponding increase in the degree of overlap of the two lines, is achieved by increasing the temperature.

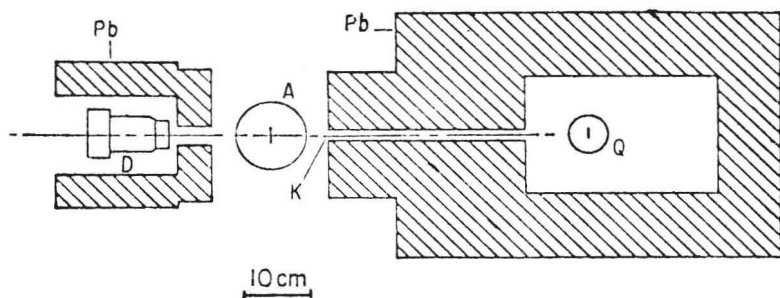


Fig. 3. Experimental arrangement. *A*, Absorber-cryostat; *Q*, cryostat with source; *D*, scintillation detector; *K*, lead collimator.

If the relative shift of the emission and the absorption lines resulting from the recoil-energy losses is only of the order of magnitude of the line widths, a temperature increase leads, under favorable conditions, to a measurable nuclear absorption effect. In the case of the 129-keV transition in Ir^{191} , there is considerable overlap of the two lines even at room temperature as a consequence of the small energies of the quanta and the small line shifts resulting therefrom (see Fig. 2). In this case, not only an increase but also a decrease in temperature can result in a measurable change in the nuclear absorption. My decision between these two possibilities was made in favor of a temperature decrease. It was motivated essentially by the consideration that at low temperature effects of chemical binding would be more likely than at elevated temperatures. This hypothesis was vindicated in an unexpected way during the course of the experiments. The simultaneous cooling of the source and the absorber with liquid air led to inexplicable results, for which I first blamed effects associated in some way with the cooling of the absorber. In order to eliminate these unwanted side effects, I finally left the absorber at room temperature and cooled only the source. In very tedious experiments, which demanded extremely stable apparatus, a small decrease in the absorption with respect to the value at room temperature was in fact obtained—a result consistent with my expectations. The evaluation of these measurements finally led to the determination of the lifetime sought for.

In a second series of experiments, I attempted to explain the side effects which had appeared in the simultaneous cooling of the source and the absorber.