Applications of the Mössbauer Effect

Volume 5

Applications in Other Fields

Edited by

Yu. M. Kagan and I. S. Lyubutin

Applications of the Mössbauer Effect

Volume 5

Applications in Other Fields

Edited by

Yu. M. Kagan
I. V. Kurchatov Institute of Atomic Energy
Moscow, USSR

I. S. Lyubutin
A. V. Shubnikov Institute of Crystallography
USSR Academy of Sciences
Moscow, USSR

Proceedings of the International Conference on
the Applications of the Mössbauer Effect
Alma-Ata, USSR, 26 September–1 October, 1983

Gordon and Breach Science Publishers
New York • London • Paris • Montreux • Tokyo

Gordon and Breach Science Publishers

P.O. Box 786
Cooper Station
New York, NY 10276
United States of America

P.O. Box 197
London WC2E 9PX
England

58, rue Lhomond
75005 Paris
France

P.O. Box 161
1820 Montreux 2
Switzerland

14-9 Okubo 3-chome,
Shinjuku-ku,
Tokyo 160
Japan

Library of Congress Cataloging in Publication Data

International Conference on the Applications of the
Mössbauer Effect (1983 : Alma-Ata, Kazakh S.S.R.)
Applications of the Mössbauer effect.

1. Mössbauer effect—Congresses. 2. Mössbauer
spectroscopy—Congresses. I. Kagan, IU. M.
II. Lyubutin, I. S. III. Title.
QC491.I537 1983 527.5'352 85-5464

Volume 5 ISBN 2-88124-060-7; 5 volume set ISBN 2-88124-030-5. Printed in Great Britain by Bell and Bain Ltd., Glasgow.

ORGANIZING COMMITTEE

Chairman
V.I. Goldanskii

Co-chairman, Chairman of Local Committee
Sh.Sh. Ibragimov

Vice-chairman, Chairman of Program Committee
Yu.M. Kagan

Vice-chairman
E.F. Makarov

Scientific Secretary
V.Ya. Rochev

Scientific Secretary
A.K. Zhetbaev

Chairman of Editorial and Publication Committee
I.S. Lyubutin

P.A. Aleksandrov, A.M. Afanas'ev, A.M. Arzhibekov, G.N. Belozerskii, V.V. Davydov, S.E. Ermatov, R.M. Gall, V.A. Grebenyuk, V.K. Imshennik, D.K. Kaipov, R.N. Kuzmin, G.A. Nekrasova, G.N. Okolovich, B.N. Pavlov, G.V. Smirnov, A.M. Voronin, S.S. Yakimov

INTERNATIONAL ADVISORY BOARD

D. Barb (Rumania), V.G. Bhide (India), T.S. Bonchev (Bulgaria), J. Cashion (Australia), J. Chappert (France), J. Danon (Brazil), H. de Waard (Netherlands), I. Dézsi (Hungary), B. Dunlap (USA), U. Gonser (FRG), D. Hanzel (Yugoslavia), R.H. Herber (USA), A. Hrynkiewicz (Poland), C.E. Johnson (UK), G.M. Kalvius (FRG), S .Mørup (Denmark), R.L. Mössbauer (FRG), Y. Nakamura (Japan), A. Simopoulos (Greece), J. Stevens (USA)

Program Committee

Yu.M. Kagan—Chairman

A.M. Afanas'ev, V.D. Gorobchenko, Yu, F. Krypyanskii, R.N. Kuzmin, I.S. Lyubutin, Yu.V. Maksimov, G.V. Smirnov, R.A. Stukan, S.S. Yakimov, B.G. Zemskov

Sponsers of the Conference

Academy of Sciences of the USSR
Acedemy of Sciences of the Kazakh SSR
The Conference was supported by the International Union of Pure and Applied Chemistry (IUPAC).

FOREWORD

The International Conference on the Applications of the Mössbauer Effect was held from 26 September to 1 October 1983 in Alma-Ata, the capital of the Kazakh Soviet Socialist Republic.

The conference was attended by about 350 scientists from 19 countries. More than 500 abstracts covering 15 scientific topics were received by the Organizing Committee, published as a book of abstracts, and distributed among conference participants prior to the conference.

In the course of the conference, 340 papers were delivered. The Program Committee selected 283 papers for publication in the conference proceedings.

The conference proceedings are published in five volumes. The first volume includes the Opening Talk by Prof. Yu.M. Kagan (USSR), 17 invited lectures, and the Concluding Remarks by Prof. V.G. Bhide (India). The invited lectures appear in the order in which they appeared at the conference.

The second through fifth volumes will contain 266 works presented as oral or poster papers, supplemented with the list of participants and index of contributors.

Mössbauer spectroscopy has made a significant contribution to various fields of pure and applied science; we believe, therefore, that the proceedings of the Conference on the Applications of the Mössbauer Effect may also be of interest to researchers working in related fields of science and technology.

THE EDITORS

WELCOMING ADDRESS

A.M. KUNAEV
President of the Kazakh SSR Academy of Sciences

Mr. Chairman, foreign and Soviet guests—participants of the Conference. Permit me to give you a cordial welcome to our capital Alma-Ata on behalf of the government and scientific community of the Kazakh Soviet Socialist Republic, to congratulate you on the inauguration of this international conference, and to wish you success in your work.

In our time, the significance of science is increasing with every passing day as is the role of the scientist in solving important contemporary problems, such as power shortages, the scarcity of raw materials, atmospheric pollution, and conflict among peoples. The second half of the twentieth century has seen major achievements in the fields of research and scientific discovery that have promoted the progress of humanity. Among such discoveries one should not fail to mention a most remarkable one, nuclear gamma resonance, discovered 25 years ago by Prof. Rudolf Mössbauer, who is now a foreign member of the USSR Academy of Sciences. During the comparatively short period since his discovery, this phenomenon has been developed extensively and at present is being successfully applied to research related to complex physical processes and the fine structure of matter. The Mössbauer effect is being used effectively to resolve many questions in the physical and chemical sciences, metallurgy, geology, biology, medicine, and engineering. This conference, which will discuss interesting results and problems concerning the further development of research on Mössbauer spectroscopy, offers eloquent proof of this versatility. Soviet scientists were among the first to assess correctly the significance of the Mössbauer effect and to engage in important theoretical and experimental research on its applications in the spheres of nuclear physics, solid state physics, chemistry, and biology. These research projects are being carried out successfully in many of our cities and scientific centers. The decision of the previous international conference in 1981 to hold the present conference in the Soviet Union testifies to this relevance. The selection of the city of Alma-

Ata as the site of the conference is also not arbitrary. The capital of Kazakhstan and the Kazakh Academy of Sciences have recently become major scientific centers where various theoretical problems related to contemporary science, as well as their practical applications, are being resolved. Through the intermediary of the Mössbauer effect, Kazakh scientists have achieved notable successes in the fields of radiation physics, solid state physics, metallurgy, biology, and chemistry. The present International Conference on the Applications of the Mössbauer Effect will undoubtedly provide new incentives to the development of research projects in science and technology.

Permit me once again to wish great success to you who are participating in this conference.

OPENING ADDRESS

Sh.Sh. IBRAGIMOV
Co-chairman of the Organizing Committee of the Conference,
Vice-President of the Kazakh SSR Academy of Sciences

Foreign and Soviet guests, colleagues, permit me, on behalf of the Organizing Committee, to inaugurate this International Conference on the Applications of the Mössbauer Effect. You are well aware that this year marks the 25th anniversary of the discovery of this remarkable phenomenon. A new type of spectroscopy based on this effect was created during this period for conducting research in the fields of dynamics and of the spatial and electronic structure of matter thanks to the work of many scientists of various nationalities. This type of spectroscopy, now known as Mössbauer or gamma resonance spectroscopy, embraces diverse fields of modern science, such as the physics and chemistry of the solid state, magnetism, and the interaction of radiation with crystals. Mössbauer spectroscopy is also widely used in biology, archaeology, and even in a number of highly specialized fields of science, such as seismogeochemistry.

The exceptional importance of this discovery is reflected in the regularity with which international conferences on this topic, in which scientists from a wide range of nations participate, are held. At the previous conference, held two years ago in India, the International Consultative Committee appointed the Soviet Union as the location for the next conference. The Academy of Sciences of the USSR duly arrived at the decision to hold the conference in Alma-Ata. We consider this a recognition of the significant contribution made by scientists of Kazakhstan to the development of Mössbauer spectroscopy, particularly as it concerns radiation effects on materials and its applications to metallurgy, chemistry, and geology. Scientists from 19 countries of the world, including the foremost specialists in this field, are participating in the present conference. They will present 510 papers on 15 different scientific aspects of this phenomenon. The Organizing Committee hopes that this conference will be held in a productive scientific atmosphere that will promote the further progress of research projects now underway in the field of Mössbauer spectroscopy.

We wish you, the participants of the conference, successful work and a pleasant stay in our city of Alma-Ata, the capital of Soviet Kazakhstan.

At the behest of the Organizing Committee, I now declare the present International Conference open.

OPENING TALK

Yu.M. KAGAN

I.V. Kurchatov Institute of Atomic Energy, Moscow, USSR

Our conference is timed to coincide with a remarkable date—the twenty-fifth anniversary of a new physical phenomenon known as the Mössbauer effect. Twenty-five years is sufficient time to look back and estimate the scale of this unique discovery and the role it has played in modern studies embracing not only physics, but also almost all fields of natural science.

The word "unique" seems to be the most appropriate one to apply to all aspects of this phenomenon. First of all, the discovery was made by a young postgraduate whose thesis examined a completely different topic—the enhancement of nuclear resonance scattering through the use of strong Doppler broadening in a crystal. The most remarkable fact is that when R. Mössbauer stumbled across the unexpected behavior of resonance scattering—it increased with a decrease in temperature—he understood its nature completely. Even in his first article twenty-five years ago, he gave a comprehensive explanation of the observed phenomenon. Moreover, in a short article published the same year, he showed, through direct experimentation, that the emission and absorption spectra of γ-quanta obtained from nuclei present in the crystal contained an excellent nonshifted line with a natural width (the recoilless line).

The Doppler shift was used at unbelievably low source velocities—on the order of centimeters per second—to reveal the resonance structure. This work therefore represents an unprecedented feat in experimental physics; it was the first direct measurement of the width of a low isomeric nucleus level. Of course, it is also unique that these first two works contain almost all the methodological fundamentals underlying all subsequent work. Looking back, we cannot help but recognize one more unique fact; the author was awarded the Nobel prize only three years after his discovery of the effect. No other work has received such international recognition within such a short time.

The most important consequence, however, is the diversity of studies based on the Mössbauer effect, which is also unique—from the analysis of the most important problems of modern physics to the study of the structural properties of materials, from the measurements of nuclear parameters to the study of ancient pottery and the ink used in medieval chronicles. Such a wide range of applications is associated primarily with the rare combination of very precise measurements at a microscopic level and a simple experimental technique. The latter has made it possible to carry out precise investigations in small laboratories and research centers, thus enlarging the role of the original scientific thinking of the individual, which was so highly esteemed earlier and which has been lost to large-scale experimental devices and enormous groups.

The number of works published on the Mössbauer effect at this time can really stagger the imagination—it amounts to 20,000. Many of these works are of a primary character. The results of other works play a strong role in the construction of the general picture in a series of various phenomena. Many of these studies were of an analytical or purely applied nature. Of course, I am not going to analyze here, even briefly, the results obtained. I should like to impart to you only some considerations which I believe are essential.

First of all, I should like to stress that the Mössbauer effect has played a crucial role in the development of general physical ideas. A whole series of complex phenomena, quite different at first glance, have been comprehended and explained by drawing an analogy using the Mössbauer effect. This held true each time we came across a system with a large number of particles subjected to a sudden external or internal stimulus and wished to determine the probability of the nonexcitation of the inner degrees of freedom in such systems; for example, the Shpol'skii effect in crystal optics. No other effect provided such possibilities for the experimental study of key problems of modern physics, such as the gravitational red shift of the earth, the Doppler effect in a noninertial system, the clock paradox, the energy-time uncertainty principle, and the conservation of space-time parity. Though these studies have not resulted in a breakthrough, they are very important, as they have enlarged the range of comparison between experiment and theory and enabled us to penetrate more deeply into the difficult problems that arose with the advent of quantum mechanics and the theory of relativity. Recent experiments, particularly those using isotopic states with longer lifetimes, lead us to believe that we have entered a period of substantially increased accuracy of measurement.

Yet the Mössbauer effect's major contribution to original physical concepts concerns the analysis of problems of coherence in the decay of long-lived isotopic states and the interactions between the Mössbauer radiation proper and the system of resonance nuclei. That the questions that may arise are sometimes of a nontrivial nature has been confirmed by many discussions. These questions will be addressed by Professor Mössbauer, who has made an attempt to revise the initial ideas of his discovery.

Let us consider, for example, the statement that a nucleus does not emit and absorb a γ-quantum instantaneously, but rather within a prolonged interval of time that is determined by the lifetime of the excited isotopic state. The space scale over which the radiation field is nonzero during decay is tens and even hundreds of meters. Even more extraordinarily, the coherence is completely preserved within time-extended nucleus decay during an arbitrary motion of the nucleus.

The lifetime of Mössbauer nuclei is abnormally long in comparison to both the characteristic nucleus time and all times typical of motion in a crystal. Here, as a rule, excited isomeric states have the most effective channel of inelastic incoherent decay—conversion of electrons. The facts that an excited nucleus does not lose its "memory" and that decay in an elastic channel correlates with incident radiation are even more interesting. Moreover, a photon whose wavelength is small in comparison to an interatomic distance is not absorbed by a single nucleus, but simultaneously by all crystal nuclei, and the phase correlation between various nuclei is preserved over its entire lifetime. As a result, the concept of a nuclear exciton—a collectively excited nucleus state smeared over a crystal—has been suggested. In fact, the lifetime of this collective excitation and the angular direction of its decay in an elastic channel were found to be very different from those in the case of a single nucleus excitation. On the other hand, it has been found that a γ-quantum traveling in a crystal and resonantly interacting with nuclei loses its vacuum properties and is transformed into a quasiparticle in a crystal. The result of this new concept is that, under certain conditions, the restructuring of the wave function of an individual γ-quantum becomes so significant that nuclear excitation in a newly formed state can completely cease; as a consequence, the channel of inelastic reaction is suppressed (conversion). Therefore, a new concept of this essentially coherent phenomenon has been formed; it is called the effect of nuclear reaction suppression in a crystal. The scale of the effect is a key factor—suppression can be complete during both the transmission in a strongly absorbing crystal and the reflection from it.

A considerable number of the phenomena described above have been verified and confirmed experimentally. As a result, a whole system of new concepts that provides an analysis of a wide range of coherent phenomena has appeared. These concepts were used in a study of the time-structure of Mössbauer radiation, particularly after resonance diffraction from a crystal, where time and spatial coherency strongly affect one another. The corresponding results formed the basis for designing pulse Mössbauer sources using synchrotron radiation. The results of the first promising experiments in this field will be presented at our conference. I should like to draw the attention of all present here to the fact that our conference is the first in which a series of works on pulse and modulation sources will be presented. These sources have a switching duration that is short or comparable with the lifetime of the nucleus.

This new technique, which at times was partially stimulated by the possibility of detecting the accelerated decay of a collective nuclear excited state in a crystal, actually has very promising experimental applications. Unlike the well-known method of delayed coincidences, it has the definite advantage of providing high intensity. It is thus possible to realize pulse Bragg diffraction of resonance radiation. This interesting method is worth a discussion of its application possibilities.

The previous statement is not accidental. Studies based on the use of the Mössbauer effect are very "flexible" and reflect changes in the orientation of research in the physics and chemistry of the condensed state. In addition to this, they effectively use, or even develop, new experimental procedures. There is one more common feature important for all studies that use the Mössbauer effect on which I should like to dwell. If we were to analyze the evolution of the works on Mössbauer spectroscopy, using their applications to solid state physics as an example, then, even with no knowledge of other works, we should obtain an adequate idea of the evolution of most of the important directions in experimentation. Mössbauer studies were initially focused on specific properties of the magnetic structures of regular systems and alloys and local properties of impurities. Attention was given to phase transitions and the specific behavior near the transition point. This gave rise to a method based on the use of Rayleigh scattering of resonance radiation.

At the same time, scientists focused their attention on interacting impurities. For example, the studies of magnetic impurities in a diamagnetic metallic matrix are pioneering works on spin-glass properties and also on the Kondo effect. Then, in accordance with the general trend in solid state physics, interest centered on the studies of the amorphous state, first in dielectrics and then in metals. I would like to emphasize the use of the Mössbauer effect in such studies, as it has significant advantages because it allows one to analyze specific features of the amorphous state at the level of the near environment. The interest in the electronic structure of irregular systems was accompanied by great attention to electronic phase transitions. This was reflected in an extensive investigation of the variable valence with the aid of the Mössbauer effect. In addition to this, metastable electronic states were also of interest, resulting in the development of emission Mössbauer spectroscopy and increased interest in the after-effects accompanying the preceding nuclear decay with filling of an isomeric state.

A great number of studies of crystal defects, especially in connection with the construction of defect structures, gave rise to the development of Mössbauer studies of implanted ions, which enabled us to investigate such properties as the structure of defect complexes, rearrangement of the environment, cluster formation, and microscopic restructuring during annealing. This branch of study is supplemented by the spectroscopy of Mössbauer atoms appearing directly in a crystal as a result of a nuclear reaction.

As we all know, intensive studies of the surface properties of solids at a microscopic level were recently initiated. This was reflected immediately in surface studies using the Mössbauer effect. An unusually accurate method of spectroscopy of conversion electrons was developed and supplemented by measurements of their energy spectra. Progress in this field is really impressive: it is now possible to study the structure of surface layers as thin as two interatomic distances. The applications of the Mössbauer effect are numerous—from the study of the electronic structure of the surface and its catalytic properties to the analysis of corrosion and the effects of surface treatment.

Until recently, the Mössbauer effect was hardly used to study superconductivity. But, with the advent of ternary alloys, where magnetism and superconductivity coexist, the Mössbauer effect has become an imporant tool in the analysis of the microscopic nature of this state.

Of course, I should like to continue this list. But it seems that even this fragmented picture demonstrates the outstanding and universal significance of the Mössbauer effect in the whole scheme of modern studies of solids.

The universal character of the Mössbauer effect is manifest in the large-scale studies of biological systems initiated in recent years. It became immediately clear which fields can use the Mössbauer effect most effectively. First and foremost, it can be used in studies of the static and dynamic structures of biomacromolecules and their conformational transitions which reveal their relation to functional activity. On the other hand, the Mössbauer effect is very useful for studying the distribution of various chemical forms of iron in proteins of lower and higher forms of life.

All of the above permits us to believe that, in celebrating the silver anniversary of the Mössbauer effect, we are witnessing an increased depth and scale of studies. An increasing number of countries carry out such studies successfully. It is not accidental that, within the last five years, international conferences on the Mössbauer effect were held in Japan and India. The conference is now being held in Kazakhstan, a Soviet republic where studies of the Mössbauer effect are carried out intensively. So it is not accidental that Alma-Ata was chosen as the site of the current International Conference on the Applications of the Mössbauer Effect. Now, I wish to express my deep and most sincere gratitude to our hospitable hosts who took the trouble to organize this Conference.

CONTENTS

Volume 5

Applications in Other Fields

Biological Systems and Model Compounds