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RESEARCH IN THE FIELD OF GAMMA-RESONANCE (MÖSSBAUER) SPECTROSCOPY*

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It is well known that nuclear physics has made great contributions to modern science and technology. On the one hand we have atomic energy, on the other the use of tracers which are included in the arsenal of literally all of the natural sciences, even archeology.

In recent years, thanks to nuclear physics, a new scientific and technological area has been discovered and rapidly developed, which is of comparable importance to the two mentioned above in its significance and range of application. This is gamma-resonance spectroscopy, based on the Mössbauer effect, [1-3] which is being used more and more extensively in physics and chemistry, in biology and geology, and for the most varied technological problems.

In this report to the General Session, I shall first speak briefly about the Mössbauer effect itself and about the fundamental characteristics of gamma resonance spectra, and then describe various applications of this new kind of spectroscopy, illustrating each direction of its development by examples from work here and in foreign countries. Particular attention will be devoted to the initiation and development of chemical gamma resonance spectroscopy, [4,5] to the problems that can be solved by it in various branches of chemistry, and particularly in biology, i.e., to the class of problems with which we have been occupied during the past few years at the Institute for Chemical Physics (ICP) of the USSR Academy of Sciences.

I. THE MÖSSBAUER EFFECT

Let us consider the Mössbauer effect, the phenomenon of recoilless resonant absorption and emission of

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γ quanta, which was discovered by Rudolf Mössbauer (of West Germany) in 1958, and which brought him the Nobel prize in physics three years later. Resonance phenomena are quite familiar because of the numerous examples in mechanics, acoustics, optics and radio engineering. In tuning our radio receiver to the waves from a sending station we change the frequency of the normal mode of oscillation of the receiver circuit and bring it into agreement with the transmitter frequency. Sometimes even a big turn of the tuning dial changes the audibility only slightly; on the other hand sometimes even the slightest touch drastically alters the reception; this means that such a resonance is sharper and more sensitive to influences.

Among the resonant receivers and transmitters there are also quantum systems: molecules, atoms and nuclei. The frequency of the radiation from such a system is given by the energy of transition E_r from the excited state to the ground state, as shown in Fig. 1: $E_r = \hbar\omega$, where $\hbar \cong 6.6 \times 10^{-16}$ eV·sec is Planck's constant. The second important characteristic of a resonance is its width Γ, which is related to the mean life τ of the excited state, $\Gamma = \hbar/\tau$. The ratio Γ/E_r characterizes the sharpness of the resonance: the smaller it is, the better the selectivity of the resonant system.

The table compares two typical resonance cases, the yellow sodium D-line and a nuclear case (transition between the excited state at 23.8 keV and the ground state in Sn^{119}). We see that the widths of the resonances for the atom and nucleus are approximately equal, but the energy of the nuclear transition is higher by four orders of magnitude. Thus the nuclear resonance is ten thousand times more selective than the atomic one; it is sufficient to change the energy of the emitted or absorbed γ quantum by at most one tril-

Characteristic parameters of typical atomic and nuclear transitions

Characteristic parameters	Atom (Na D-line)	Nucleus (Sn[119])
Transition energy E_r, eV	2.1	23 800
Lifetime of excited state, τ, sec	$1.5 \cdot 10^{-8}$	$2.7 \cdot 10^{-8}$
Natural width of level, Γ, eV	$4.4 \cdot 10^{-8}$	$2.4 \cdot 10^{-8}$
Sharpness of resonance, Γ/E_r	$2.1 \cdot 10^{-8}$	10^{-12}
Recoil energy of atom or nucleus R, eV	10^{-10}	$2.5 \cdot 10^{-3}$
Ratio of recoil to transition energy R/E_r	$\sim 5 \cdot 10^{-11}$	$\sim 10^{-7}$
Ratio of recoil energy to level width R/Γ	$\sim 2.3 \cdot 10^{-3}$	$\sim 10^{5}$

lionth part to destroy or establish the resonance conditions. But an accuracy of one part in a trillion corresponds, for example, to measuring the radius of the whole solar system to an accuracy of the height of a two-story house. It is easy to see why the prospects of observing γ ray resonance seemed so attractive. But it is just this extreme selectivity of such a resonance that, together with the high energy of γ quanta, for decades prevented its observation.

The point is that in emerging from the nucleus (or atom), the γ quantum (or light quantum) sort of pushes away from it, leaving the nucleus (or atom) to move in the opposite direction. Such a recoil takes up an energy $R = E_r^2/2mc^2$, where m is the mass of the radiator and c is the velocity of light. In the atomic case the recoil energy is much less than the width of the resonance ($R \ll \Gamma$), so the occurrence of recoil does not spoil the observation of resonance phenomena. The situation is entirely different for nuclei: the recoil energy is higher by factors of hundreds of millions, and the emission line, shifted toward lower frequency ($E_r - R$), is an amount 2R away from the position of the absorption line at ($E_r + R$), since the absorbing nucleus when excited by an amount E_r also acquires the additional kinetic energy of recoil R. Resonance is possible only because of partial overlap of the two lines that have been separated by the recoil, and that are also distorted because of the thermal motion of the nuclei and the associated Doppler shift in the frequency of the γ quanta.

Recoilless nuclear gamma resonance (NGR for

short) was discovered by Mössbauer under conditions where the emitting and absorbing nuclei (Ir[191] in his first experiment) were in a crystal lattice, being held together by millions of similar chains of chemical bonds. The recoils during emission or absorption are unable to break these links, and so the recoil energy can be used only to excite quanta of vibration of the atoms in the lattice—phonons. It can also happen, especially at low temperatures, that no phonon excitation occurs.* Then the lattice as a whole experiences the recoil, so in the expression for the recoil energy the denominator contains not the mass of an individual nucleus but rather the mass of the lattice. Just as in the firing of an infinitely heavy gun, the recoil energy tends to zero, becomes smaller than the width of the resonance ($R \ll \Gamma$), and does not prevent observation of the resonance. On the background of the shifted and broadened spectra of emission and absorption, whose maxima are separated because of recoil by an amount 2R, there appears, as shown in Fig. 2, an intense unshifted and unbroadened resonance line.

It is interesting that in explaining the results of his experiments Mössbauer based his argument on the theory of the appearance of a similar line in experiments on neutron scattering, which was given by Lamb 20 years before the discovery of recoilless nuclear γ ray resonance. During a period of twenty years the Mössbauer effect was not discovered because experimenters working with γ rays never thought about the theory being applied literally next door, while scientists working on interactions of neutrons with solids never thought about the related problems for γ quanta. Here is a clear example of the harm done by overspecialization!

It is clear from our remarks that a nuclear resonance line with its natural width is a measuring instrument of the highest precision.

But how is one to make use of this instrument, how is one to observe the Mössbauer effect experimentally and study it quantitatively? First one needs a transmitter and receiver, the roles being played respectively by a radiating nucleus and a stable isotope of the
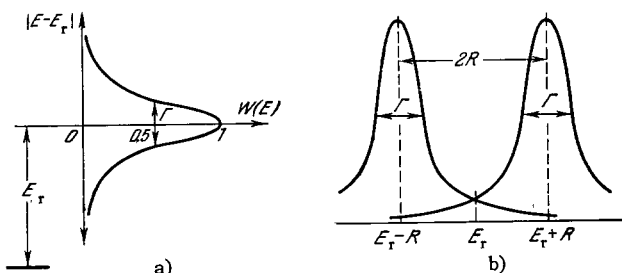

FIG. 1. Illustration of Resonance. a) Excitation probability W(E) as a function of deviation of energy transfer from its resonant value E_r(Γ is the natural width of the resonance); b) resonance lines for radiator and absorber, shifted values lower and higher than E_r, respectively, by the amount of the recoil energy R = $E_r^2/2mc^2$.

*The probability of the effect, f', according to the Debye approximation, is given by the formulas in the legend of Fig. 2. The quantity θ is the Debye temperature, and at high temperatures (T >> θ) f', tends to zero.
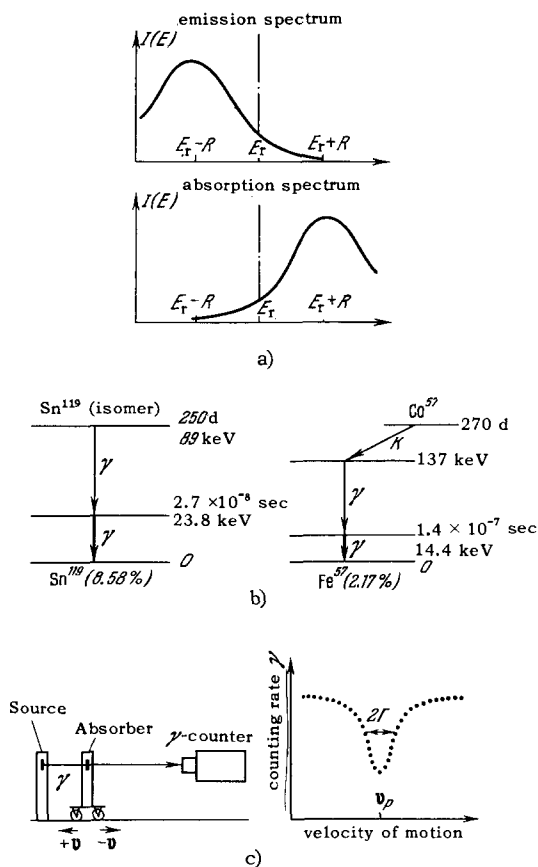
FIG. 2. Illustration of the Mössbauer Effect. Emission and absorption spectra of γ quanta. On the background of the displaced and broadened spectra, one sees a resonance line with the natural width (shown on a scale of 1:200 for the case of Ir^{191} at $88°K$). The formulas characterizing the probability of the Mössbauer effect in the Debye approximation (θ is the Debye temperature) are:

$$f = \exp\{2W(T)\}, \quad T \ll \theta: \quad W = \frac{3}{4}\frac{R}{k\theta},$$

$$T \gg \theta: \quad W = \frac{3}{4}\frac{R}{k\theta}4\frac{T}{\theta} \quad (W \gg 1, f \to 0).$$

b) Decay schemes of Sn^{119} and Co^{57}—Fe^{57}. The figures give the half-lives, transition energies, and percentage content of Sn^{119} and Fe^{57} in the normal mixtures of isotopes of tin and iron. c) Schematic of experiment for recording γ resonance spectra, i.e., the dependence of the γ quantum counting rate on the velocity of motion of the absorber (or source), and a typical form of such a spectrum; the velocity is

$$v \approx c\Gamma/E_r \approx (10^{-12} \div 10^{-15})c = 10^{-2} \div 10^{-5} \text{ cm/sec.}$$

same isotope—the resonance absorber of the γ quanta. Figure 2 shows the decay schemes of two nuclei that are extensively used in nuclear gamma spectroscopy—Sn^{119} and Fe^{57} (which is formed after K capture by the parent nucleus Co^{57} in the radiation source).

In addition one must change the energy of the γ quanta in a controlled way. Everyone knows that when a source of sound moves, the frequency or tone of the emitted sound signal changes, though not everyone knows that such a change is only one of the manifestations of the so-called Doppler effect. This same effect is also used for changing the energy of the quanta in the

NGR method, where because of the extreme sharpness of the resonance one requires a completely negligible motion of the absorber relative to the source: v $= \Gamma c/E_r$, which depends on the value of Γ/E_r, i.e., on the properties of the particular nucleus, varying from fractions of a mm/sec (Sn^{119}, Fe^{57}) even to fractions of a μ/sec (Zn^{67}).

The schematically pictured experiment on the dependence of the counting rate of γ quanta radiated by the source on the velocity of the absorber placed between the source (the radiator) and the counter is the basic experimental procedure of gamma resonance spectroscopy. A typical form of this dependence, which is called a gamma resonance or Mössbauer spectrum, (NGR spectrum) is shown in Fig. 2. The resonance peak or line corresponds to a minimum in the counting rate, i.e., to maximum absorption near some particular absorber velocity. Thus, experiments on gamma resonance spectra consist in setting in motion the source or absorber, and thus compensating all sorts of external factors that influence the energy of the resonance transition, and then quantitatively studying these factors. Mössbauer's discovery thus provided a method for the most exact recording of energies or γ quanta. But the mere existence of this possibility, which is the basic instrument for future gamma resonance spectroscopy, did not yet mean that it had been developed. It seemed at first that the phenomenon that had been discovered applied only to a rather small range of problems in nuclear physics. In formulating the new directions for spectroscopy, in extending its use to solid state physics, chemistry, biology, geology and engineering, many scientists from different countries took part, and the work of Soviet scientists was of great importance.

II. PARAMETERS OF GAMMA RESONANCE SPECTRA

Since our school days we have become accustomed to the assertion that any transformation of nuclei is independent of external conditions such as temperature, pressure and chemical environment. But at the level of accuracy of measurement of γ ray energies that is achieved by the Mössbauer effect, such an assertion becomes quite meaningless. The motion of atoms in molecules and crystal lattices, the interaction of the charge, electric and magnetic moments of a nucleus with the surrounding electron cloud—all of these affect the energy of the γ quanta, and all can consequently be studied by the method of gamma resonance spectroscopy.

Figure 3 gives a schematic listing of the parameters of Mössbauer spectra and the information they contain.

Let us start with the "Mössbauer probability" f', which appears in an experiment as the area under the resonance peak (Fig. 3a). The value of f' characterizes the extent of the thermal motions of the atoms in
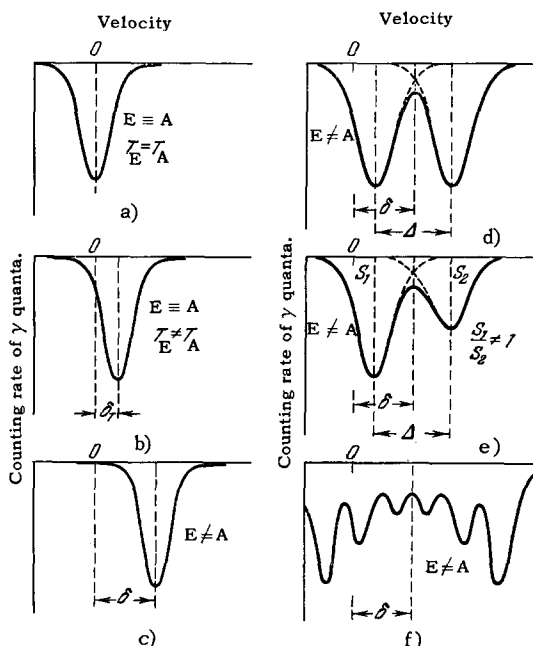
Velocity   Velocity

FIG. 3. Parameters of gamma resonance spectra and information obtainable from them (E - emitter, A - absorber). a) The peak area gives $\bar{r}^2$; $f'(T) \propto \exp(-\bar{r}^2/X^2)$; diffusion affects the width of the line; b) the temperature shift of the line characterizes $\bar{v}^2$: $\delta_T \cong E_r\bar{v}^2/2c^2$; c) the isomer (chemical) shift of the line

$$\delta \propto [|\psi(0)|_A^2 - |\psi(0)|_E^2]\Delta R/R$$

characterizes the density $|\psi(0)|^2$ of electrons in the region of the nucleus, i.e., is related to the s-electrons; d) the quadrupole splitting Δ characterizes the gradient of the electric field $q = \partial^2 V/\partial z^2$ in the region of the nucleus, i.e., is related to the p- and d-electrons; e) asymmetry of the quadrupole splitting may be caused by anisotropy of the thermal vibrations of the Mössbauer atoms $(\bar{x}^2 \neq \bar{y}^2 \neq \bar{z}^2)$ or effects of paramagnetic relaxation; f) magnetic splitting characterizes the strengths of local magnetic fields near the positions of the nuclei, resulting from polarization of the inner s-electrons. The nature of the magnetic splitting depends critically on the paramagnetic relaxation time and on the magnetic ordering of the material.

molecules and lattices—their mean square amplitude $\bar{r}^2$.

A detailed theory relating the value of f' and its temperature dependence to the spectrum of vibration frequencies of a complex lattice was developed by Yu. M. Kagan (I. V. Kurchatov Atomic Energy Institute (AEI)).[6,7] An important part of this theory is the treatment of the effect on the recoilless resonance probability of the so-called optical branches of the vibrations, which have quite high energies (and consequently, small amplitudes), and which, in the long-wave approximation, characterize the motion of atoms relative to their nearest neighbors, in contrast to the simultaneous displacements of many atoms that appear in the acoustic branches. The presence of the optical branches is of importance because they make it possible to observe gamma resonance spectra in systems that contain light atoms (this is of particular impor-

tance for chemistry) and at quite high temperatures. The theory also predicted a possible anisotropy of the Mössbauer effect on single crystals,[8] related to the difference of the amplitudes of atomic vibrations along different crystal axes $(\bar{x}^2 \neq \bar{y}^2 \neq \bar{z}^2)$. Such an anisotropy was actually soon detected in joint experiments of the Institute for Physical Problems (IPP) and the Nuclear Physics Research Institute (NPRI) of Moscow State University.[9] We mention that not only the area, but also the width of the resonance line, gives definite information characterizing the diffusion of the atoms.[10,11] Suppose that in our first example (cf. Fig. 3a) the radiator and absorber are chemically identical and are kept at the same temperature. The absorption maximum then corresponds to having the absorber at rest: $v = 0$. If we now change the absorber temperature from T_0 to T_1, the position of the absorption maximum is shifted by an amount δ_T, as shown in Fig. 3b. This shift (the temperature shift of the line) characterizes the mean kinetic energy of vibration of the atoms in the lattice, i.e., their mean square velocity $\bar{v}^2$.

A very important parameter is the isomer (chemical) shift of the line δ (cf. Fig. 3c), caused by the difference in the chemical state of the atoms of the emitter and absorber, and first discovered by Kistner and Sunyar[12] for various compounds of iron. The isomer shift arises because of the change in energy of electrostatic interaction between the electric charges of the nucleus and the electron shells, and is determined by the product of two quantities, one of which $(\Delta R/R)$ is of nuclear origin (relative change of the charge radius of the nucleus on excitation) while the other is atomic or molecular. This quantity—the difference between the squares of the wave functions (i.e., the densities) of the electrons at the nucleus in the absorber and emitter, is of particular interest for chemists, since it characterizes the structure of the so-called s-electron shells and the participation of the s-electrons in chemical bonds. Interesting calculations of nuclear and atomic or molecular parameters have been made in our country for the example of tin. The nuclear calculations[13] were based on the theory of finite Fermi systems developed by A. B. Migdal; the atomic-molecular calculations were made at the ICP using the molecular orbital method.[14,15] The main conclusions of the two methods of calculation are identical, which raises one's confidence in these quantitative computations of properties of chemical bonds for a wide class of compounds.

The interaction of the electric quadrupole moment of the nucleus (in its ground and/or excited state) with an inhomogeneous electric field gives rise to a quadrupole splitting Δ of the gamma resonance lines (cf. Fig. 3d), which is proportional to the product of the quadrupole moment Q and the electric field gradient q. Of these two quantities the first is again a

nuclear quantity, while the second is atomic or molecular, characterizing the properties of the p- and d-shells of electrons. The possibility of separate description of the participation of s-, p- and d-electrons in chemical bonds by an examination of isomer shifts and quadrupole splittings is a very important advantage of chemical gamma resonance spectroscopy, which allows one, for example to distinguish between the roles of changes in degree of ionicity and hybridization of chemical bonds.

Often the quadrupole splitting is asymmetric even for completely isotropic polycrystalline samples, as is shown in Fig. 3e. Such an integral asymmetry in the areas of the two peaks was first discovered and investigated in detail for various examples by the group at the ICP of the Academy of Sciences of the USSR[16,17] and interpreted by S. V. Karyagin[18] of the same institute. This asymmetry is a consequence of the anisotropy mentioned above, that occurs in the crystallites ($\overline{x^2} \ne \overline{y^2} \ne \overline{z^2}$), and its observation opens the possibility of studying structural features of single crystals, without growing them, from experiments on polycrystals (which is somewhat analogous to taking Debye-Scherrer patterns). An important point is that the investigation of the "anisotropic" asymmetry of the quadrupole splitting and its explanation floundered among confused trivial assumptions (for the last of these relapses, cf.[19]) about superpositions of spectra from various hypothetical impurities or structural isomers, which to some extent hindered the development of chemical gamma resonance spectroscopy. There is also another possible origin of the asymmetry of the quadrupole splitting, related to the interaction between the electric and magnetic fields produced at the nucleus by unpaired electrons in the atom.[20] Such a "paramagnetic" asymmetry (I emphasize that this is for paramagnets) appears more strongly the longer the paramagnetic relaxation time, i.e., the slower the turning of the electron spins. Thus, unlike the "anisotropic" asymmetry of the quadrupole splitting, the "paramagnetic" asymmetry becomes weaker with increasing temperature.

Ordered or very slowly relaxing unpaired electrons of outer shells give rise to a polarization of the inner electrons, and thus destroy the complete compensation of the magnetic effects of the antiparallel spins of the two s-electrons in the shell closest to the nucleus. As a result there are enormous magnetic fields in the interior of the atom, which can be measured by using the magnetic (Zeeman) splitting of gamma resonance lines (cf. Fig. 3f).

The theory of the magnetic splitting of nuclear gamma resonance lines was also developed in detail by Yu. M. Kagan and A. M. Afanas'ev.[21] Here a whole variety of cases are possible—from a single line to a definite hyperfine structure. The form of the spectrum is affected by the temperature, the widths of individual peaks associated with the paramagnetic relaxation time, and, of course, transitions from the paramagnetic to the ferro- or antiferromagnetic state.

A special area of the work on gamma resonance is the theory of coherent phenomena[22,23] (cf. also [24]), for example, the suppression of the absorption of γ quanta in an ordered array of nuclei as compared to that in an individual nucleus or an irregular system. As a result of such a suppression, the lifetime of the excited state of a nucleus in a regular lattice may be greater than in the free state, i.e., the width of the excited level is less than the natural width of the line. It is possible, on the other hand, to have a shortening of the lifetime, with speedup of the decay. Problems of coherent effects in the radiation and propagation of γ quanta, whose wavelengths are ten thousands of times smaller than that of visible light, are naturally of very great interest. There is no doubt that any future advances in the solution of these problems will have the closest connection with the Mössbauer effect.

Present investigations of the structure of matter are characterized by an astounding variety in the experimental techniques used. Optical spectroscopy, EPR, nmr and quadrupole resonance methods of radiospectroscopy, x-ray analysis, electron and neutron diffraction, scattering of cold neutrons,—it is difficult to enumerate all the methods, to which we now add gamma resonance spectroscopy. Of course, no one of these methods is a panacea, destined to solve all the problems of the structure of crystals and molecules. In this respect the nuclear gamma resonance method, with all its richness of possibilities, is no exception. Our problem is not to pit one method against another; there is no question of competition, but rather of mutual assistance of different methods. It is therefore extremely desirable to add the gamma resonance method to the others.

The most important limitation of gamma resonance spectroscopy is that the Mössbauer effect is observed only in the solid phase and in not too many elements. In particular, because of the increase in energy of the low-lying levels as the mass of the nucleus decreases, the recoil energy for free nuclei of light elements is so large that the effect is vanishingly small for them. So far the lightest element showing the Mössbauer effect is potassium. All the elements for which a Mössbauer effect has been observed are shown in Fig. 4. One must say that the list of thirty elements given in the figure (including iron, nickel, zinc, tin, tellurium, iodine, krypton and xenon, almost all the lanthanides, and neptunium) is far from exhaustive.

Despite the absence from the list of "Mössbauer" elements of such abundant elements as carbon, nitrogen, oxygen and silicon, the range of applications of gamma resonance, as we shall soon see, is extremely broad, and is even further extended by the use in many cases of gamma resonance nuclei as "indicators" to characterize the properties of systems into which they are specially introduced. We shall now go on to con-
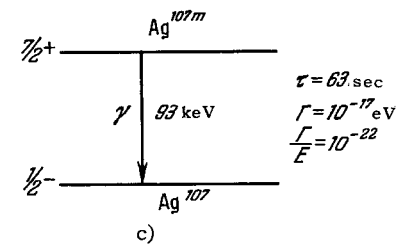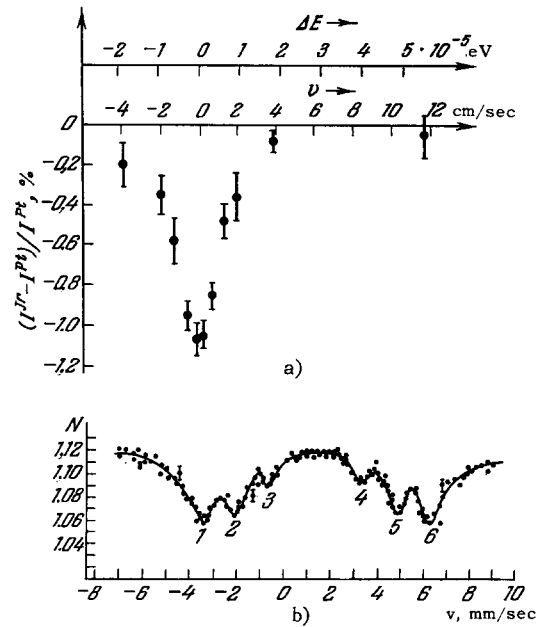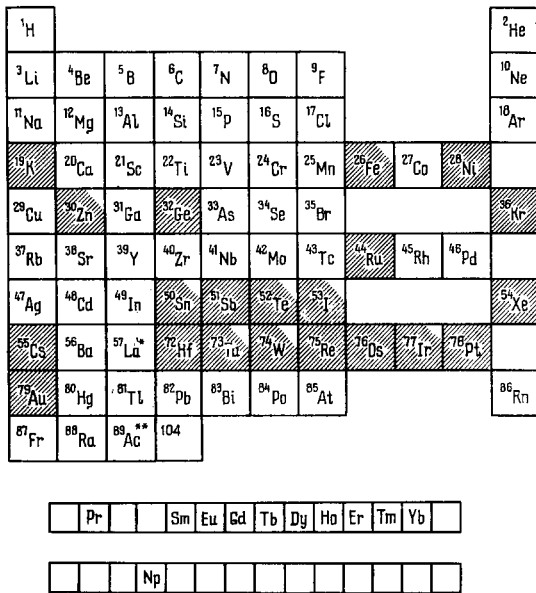
FIG. 4. Elements for which the Mössbauer effect has been observed are cross-hatched. A bright upper right corner of a shaded box means that the effect has been seen at room temperature. The effect should be seen in almost all the lanthanides and actinides; the insertion of the chemical symbol in certain boxes for these families of elements means that the effect has already been observed. Silver is not cross-hatched; the ratio Γ/E_r is particularly small (10^{-22}), so that experiments on Doppler shifting to vary the gamma resonance absorption have not been done.

FIG. 5. Applications of the Mössbauer effect (recoilless gamma resonance) in nuclear physics. a) NGR spectrum of Ir^{119} (determination of lifetime); [1-3] b) NGR spectrum of Sn^{119} in FeSn (determination of magnetic moment of the excited Sn^{119} nucleus ($\mu_{Sn^{119}}$ - 0.68 n.m.); [25] c) decay scheme of isomeric state of Ag^{107} (direct excitation of isomeric state of Ag^{107}). [26]

sider concrete proofs of the fruitfulness of gamma resonance spectroscopy in various branches of science and technology. Without striving for a complete summary of the data, we shall illustrate each field by a few of the important and, if possible, easily visualized examples.

III. SOME APPLICATIONS OF THE NGR METHOD TO NUCLEAR AND GENERAL PHYSICS

Let us start with nuclear physics, the science which gave us the Mössbauer effect.

The first of the examples shown in Fig. 5 is taken from early work of Mössbauer himself[2,3] with Ir^{191}. Because of the Heisenberg relation, the determination of the width Γ of the gamma resonance line gives direct information about the mean life τ of the excited nucleus. In this way it was found that for Ir^{191}, $\tau = 1.4 \times 10^{-10}$ sec (Fig. 5a).

Data on quadrupole and magnetic splitting of lines in gamma resonance spectra enable one to determine the electric and magnetic moments of excited nuclei, despite their extremely short lifetime. In this way one found, for example, that the Q of the 14.4 keV excited state of Fe^{57} ($\tau \approx 1.5 \times 10^{-7}$ sec) is Q = 0.15, and that the magnetic moment of the 23.8 keV excited state of Sn^{119} ($\tau \approx 2.7 \times 10^{-8}$ sec) is $\mu = 0.68$ n.m.

The shape of the NGR spectrum of tin in $FeSn_2$, obtained by NPRI[25] and used to determine μ for Sn^{119},

is shown in Fig. 5b. A record result was the discovery by N. A. Burgov et al at the Institute for Theoretical and Experimental Physics (ITEP)[26] of the direct excitation of the very longlived isomeric state of Ag^{107} (cf. Fig. 5c) when an inactive sample was irradiated with resonance gamma quanta. In this case the ratio that characterizes the selectivity of the resonance is $\Gamma/E = 10^{-22}$(!), i.e., the resonance is ten billion times sharper than for tin. A most impressive result is that of the Americans Pound and Rebka,[27,28] which was proposed independently by the Soviet scientists I. Ya. Barit, M. I. Podgoretskiĭ and F. L. Shapiro.*

The schematic of this experiment is shown in Fig. 6. Suppose that a radiator is at the top of a tower, at a height h, while the absorber is below on the ground. When a body of mass m falls from a height h its potential energy mgh is converted to kinetic energy. The ratio of this additional energy to the total energy

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*Reference[29] first stated the general problem of possible applications of the Mössbauer effect to measuring small energy shifts.

Radiator   Radiator
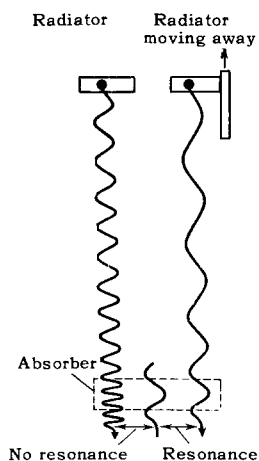   moving away

Absorber

No resonance   Resonance

FIG. 6. Illustration of the experiment of Pound and Rebka,[27] demonstrating the increase in energy of a gamma quantum falling through the gravitational field of the Earth:

$$\Delta E = mgh, \quad E = mc^2,$$
$$\Delta E/E = gh/c^2 \cong 10^{-16} \text{ m}^{-1}.$$

of the body, which according to Einstein is equal to mc^2, is obviously $\Delta E/E = mgh/mc^2 = gh/c^2$. This ratio is independent of the rest mass m and should, according to the theory of relativity, also apply to γ quanta, which have no rest mass. In falling from a height h = 20 m, a γ quantum should become "heavier" by a fraction 2×10^{-15}—this will be the increase in its energy or frequency. As a result the conditions for gamma resonance are somewhat spoiled, and to compensate one must move the radiator upward, away from the absorber, at a velocity of $2 \times 10^{-15} c = 6 \times 10^{-5}$ cm/sec. The experiment, using Fe^{57} nuclei as radiator and detector, precisely confirmed the predictions of the Einstein theory, and enabled them to "weigh" the quanta of electromagnetic radiation several years earlier than people had proposed to do by means of artificial earth satellites and laser generators of radio waves.

IV. SOME APPLICATIONS OF NGR TO SOLID STATE PHYSICS

Of all the branches of physics, the one in which the Mössbauer effect gave and continues to give the richest information is solid state physics. Here are some convincing proofs. By embedding tin in vanadium and observing the temperature dependence of the probability for gamma resonance, V. A. Bryukhanov and N. N. Delyagin[30] (NPRI) in collaboration with Yu. M. Kagan compared this dependence (Fig. 7a) with that calculated from the theory of the vibrations of an impurity atom in a cubic lattice.[8] The spectrum of vibrations of the vanadium host lattice that is needed for such computations was found independently in the AEI from experiments with cold neutrons. The beautiful agreement of computations and experiment demonstrates the great possibilities of quantitative gamma resonance spectroscopy of simple and complex crystal lattices.

We have already stated that the interaction of unpaired electrons of the outer shells with the inner s-electrons can, under certain conditions, lead to the appearance of extremely strong local magnetic fields

f'

H_n,MOe

a)   b)

$H_n(\text{Fe}) = f(T^\circ)$

H_n kOe

$\Gamma(Sn) = f(T^\circ)$
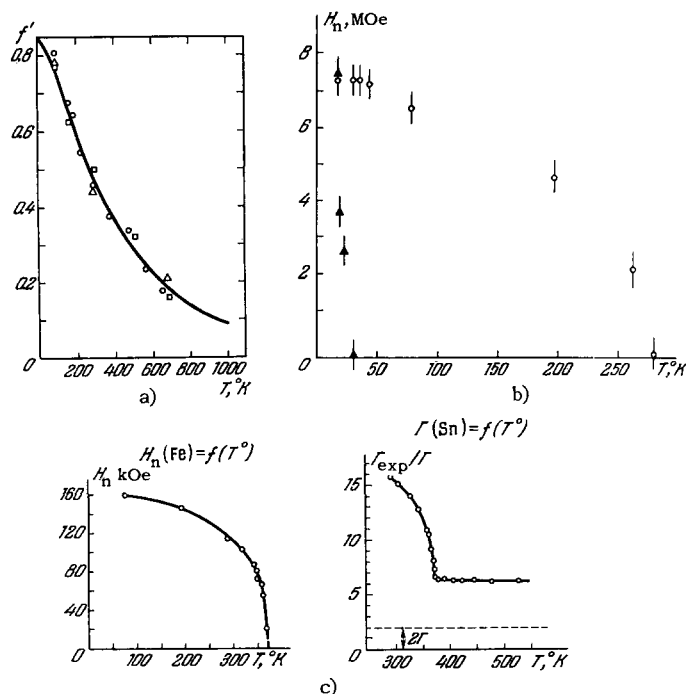
Γ_{exp}/Γ

c)

FIG. 7. Applications of the Mössbauer effect to solid state physics. a) Temperature dependence of the Mössbauer probability f' for tin nuclei embedded in vanadium;[30] b) temperature dependence of the magnitude of the local magnetic field at Dy^{161} nuclei in metallic Gd; $H_{n(0)} \approx 7.3 \times 10^6$ Oe;[31] c) temperature dependence of local magnetic field at iron nuclei and line width in NGR spectrum of tin in $FeSn_2$.

at the position of the nucleus. The magnitude of these fields is determined directly from hyperfine structure of the NGR spectra, since the magnetic moment of the absorbing nucleus (i.e., the nucleus in its ground state) is usually known from other experiments. Figure 7b shows a recent study at the AEI[31] of the temperature dependence of the field at Dy^{161} impurity nuclei which are formed in a lattice of metallic gadolinium as the result of neutron capture and two successive β decays. At 5°K the local magnetic field in this case reaches a value of 7.3×10^6 Oe. Judging from the falloff of the field with temperature, there are two states of dysprosium; for the first the local field vanishes near 20°K, while for the second it vanishes when the gadolinium itself ceases to be ferromagnetic (Curie temperature around 290°K).

In this same institute, in the laboratory of I. K. Kikoin,[32] it was demonstrated that there is a clear correlation between the magnetic fields at the nuclei and the spontaneous magnetizations of the sublattices of the antiferromagnet $FeSn_2$. The magnetic fields were determined for both the iron and tin (cf. Fig. 7c), for the iron directly from the splitting of the line, for the tin from the width of the unresolved hyperfine structure (this width decreases with decreasing local field at the nucleus).
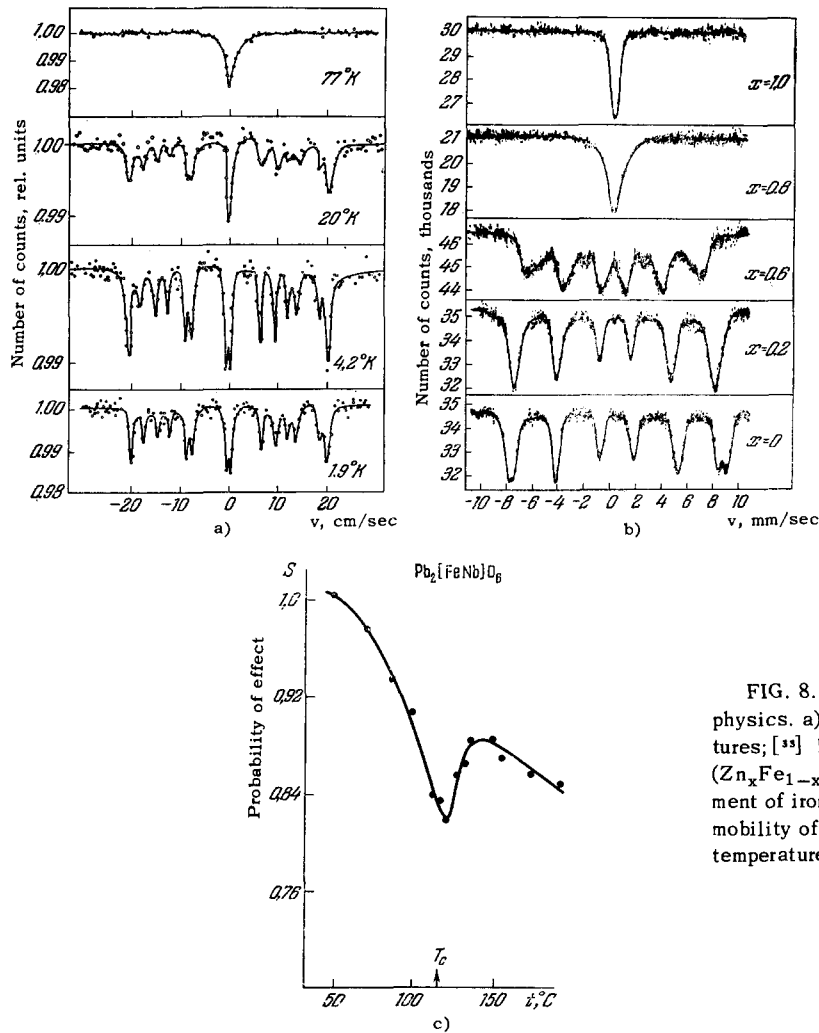
A disordering of the electron spins or their con-

FIG. 8. Applications of the Mössbauer effect to solid state physics. a) NGR spectrum of Dy + Al garnet at different temperatures; [33] b) NGR spectrum of Fe^{57} in Ni + Zn ferrite-spinels $(Zn_xFe_{1-x})[Ni_{1-x}Fe_{1+x}]O_4$ for different degrees (x) of replacement of iron in the tetrahedral lattice by zinc; [34] d) increase in mobility of atoms in the lattice of a ferroelectric near the Curie temperature (114°). [35]

tinual rapid reorientation leads, of course, to the disappearance of the magnetic hyperfine structure (hfs) of NGR spectra, since the time average of the local field at the nucleus then becomes equal to zero. The general theory of gamma resonance in systems with unpaired electrons, [21] which takes all these facts into account, has been tested and verified on many examples. We shall limit ourselves to demonstrating two extremely graphic cases of a change in the character of NGR spectra in such systems.

Figure 8a shows some observations by the Americans [33] of the spectrum of dysprosium (Dy^{161}) in dysprosium-aluminum garnet, which is antiferromagnetic at temperatures below 2.49°K and paramagnetic above that temperature (the so-called Néel point). The transition to the paramagnetic state itself does not give rise to any sharp change in the hfs. It drops only gradually, because of the drop in the electron relaxation time, i.e., the speeding up of the reorientation of the spins with increasing temperature. Such a speedup also leads, in accordance with the theory, to a broadening of the hfs.

Figure 8b shows the spectra obtained in the ICP [34]

for nickel-zinc ferrite spinels $(Zn_xFe_{1-x})[Ni_{1-x}Fe_{1+x}]O_4$, complex oxides that are a kind of salt of an iron acid. Here the iron enters in two sublattices, tetrahedral and octahedral, whose interaction causes the appearance of uncompensated antiferromagnetism, or what is called ferrimagnetism.

As the iron is bound more tightly into the tetrahedral sublattice by the zinc ions, the exchange interaction between the sublattices weakens, and the ferrimagnet is transformed into a paramagnet with very short spin-lattice relaxation time, while the magnetic splitting of the spectral line disappears. It should be stated that the properties of ferrites—ferrimagnetic dielectrics or semiconductors, are not only of theoretical, but also of practical, interest. These materials, whose magnetization even at high frequencies is not accompanied by large energy losses to eddy currents, are now used very widely in automation and telemechanics, in high-frequency and pulsed radio equipment, and in computers.

Of similar two-fold interest is the application of the Mössbauer effect to studying still another class of materials—ferroelectrics, which have a dielectric

FIG. 9. Applications of the Mössbauer effect to solid state physics. a) NGR spectrum of Fe^{57} in dilute alloys $Fe_{0.05}Au_{0.95}$ with and without an external axial magnetic field;[37] b) change of local field at Fe^{57} nuclei in FeAl alloy as a function of average distance between iron atoms and nearest impurity aluminum atoms (showing the role of indirect interaction through the conduction electrons) c) NGR spectrum of Sn^{119} in yttrium-iron garnet $\{Y_{3-x}Ca_x\}$ $[Sn_xFe_{2-x}](Fe_3)O_{12}$ (above) and temperature dependence of local magnetic fields at Fe nuclei in the two sublattices and at the Sn nuclei, at various temperatures (below), and also the conductivity of the garnets (upper right of lower figure).
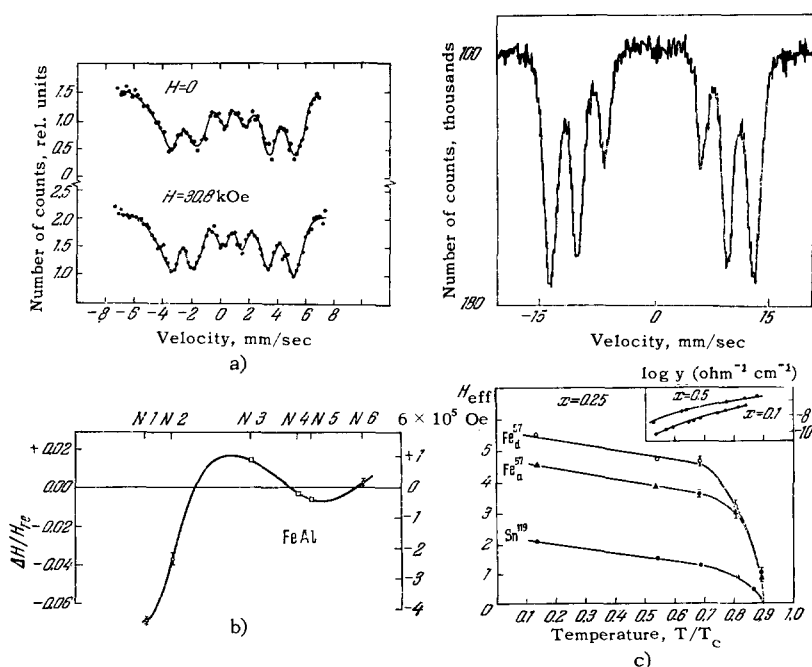
polarization even in the absence of an external electric field. The electric properties of ferroelectrics are in many ways similar to the magnetism of ferromagnets. Typical for both is the existence of a definite critical temperature (the Curie temperature) above which the thermal motion destroys the ordering of the electric or magnetic moments, and the ferroelectric or ferromagnetic properties disappear. Ferroelectrics are also used in all the areas enumerated above for ferrites.

V. V. Sklyarevskii et al[35] discovered a marked increase in mobility of atoms in the lattice of a ferroelectric near the point of transition from the ferroelectric to the paraelectric state—a phase transition of the second kind. In fact, we see from Fig. 8c that near the Curie temperature (114°C) there is a marked decrease in the probability for the Mössbauer effect on the iron in the ferroelectric $Pb_2[FeNb]O_6$. Observations of the Mössbauer effect also have enabled the discovery of completely new phenomena.

Thus, in the work of American physicists[36,37] there was observed a magnetic ordering of the electron spins in an extremely dilute solution of iron (5%) in gold (95%). The constancy of the hfs as to number of lines, their width and splitting (cf. Fig. 9a) when an external axial magnetic field is applied (up to 3 × 10^4 Oe) indicates that the spin ordering in this alloy is antiferromagnetic. Thus, here we have what is called indirect or super-exchange interaction between unpaired electrons, not through homopolar bonds, as in various magnetic oxides or in ferrites, but via the conduction electrons.

The quantitative study of indirect interaction between 3d-electrons of iron via the 4s conduction electrons was made in experiments of another Ameri-

can group[38] with small admixtures of aluminium to iron. Figure 9b shows the change in the field at the iron nuclei as a function of the average distance between the iron atoms and their nearest aluminium impurity atom. It was found that the spin density of the conduction electrons at the iron nuclei in ferromagnetic alloys of the FeAl type oscillates, and that the contribution of the indirect exchange interaction for pairs of nearest neighbors is antiferromagnetic and leads to a decrease of the magnetic field in the region near the nucleus.

An even more peculiar example of indirect magnetic interactions was the independent discovery a year ago by two groups of Soviet scientists, at the ICP[38] and at the Institute for Crystallography,[40] of superexchange induction of magnetic fields at the nuclei of diamagnetic tin atoms in $\{Y_{3-x}Ca_x\}[Sn_xFe_{2-x}](Fe_3)O_{12}$ yttrium-iron garnets. The NGR spectrum of such a garnet, obtained at the ICP, is shown in Fig. 9c. The parameters of the spectrum: the chemical shift (equal to the shift for SnO_2), the quadrupole splitting (which is absent in this case, indicating equality of all the Sn bonds), the probability of the effect and its temperature dependence, forced the conclusion that the tin has no direct bonds to the iron, but is bound to it through the oxygen: Sn—O—Fe. Nevertheless, as one sees from the Zeeman splitting of the spectral line into six components, there is at the nucleus of the diamagnetic tin atom a considerable magnetic field*, more than 2 × 10^5 Oe at 77°K, which

*Later experiments carried out at the ICP by the authors of[39] showed that the sign of this local magnetic field agrees with the sign of the applied external axial magnetic field.

vanishes at the Curie point simultaneously with the vanishing of the field at the iron nuclei (cf. Fig. 9c). Measurements of the conductivity and its temperature dependence showed that the action of the unpaired electron in the iron could not be transmitted to the tin nucleus through the conduction electrons.

It was thus established that the unpaired electron in the iron, acting through the two chemical bonds Fe—O and O—Sn, polarizes the inner s-electrons of the Sn

via superexchange interaction, and thus causes the appearance of a field at the nucleus.

In other words, they found a delocalization of the unpaired electron of the iron in an inorganic system, having only σ bonds, and found that this delocalization is manifested in a polarization exchange interaction of the unpaired electron with the inner s-shells.

V. EXAMPLES OF CHEMICAL APPLICATIONS OF GAMMA RESONANCE SPECTROSCOPY

The last example has already led us to some extent to chemistry, to which we now turn. Chemistry is probably the field in which the NGR method has now become most important. The domain of chemical applications of the Mössbauer effect is continually and rapidly increasing. Work on a variety of developments and applications of chemical gamma resonance spectroscopy were started at the ICP of the USSR Academy of Sciences about five years ago. During the first few months we worked with the apparatus of the NPRI of Moscow State University, which was doubly advantageous: it enabled us to start experiments on our program even before producing our own gamma resonance spectrometers, and also enabled us later to do some of these investigations not only in the ICP, but also at the NPRI, even though the latter is not a chemical institute.

In our first experiments, carried out with compounds of tin, mainly tin-organic compounds, we obtained several results that formed the general basis for chemical gamma resonance spectroscopy. Thus, we found the presence of a Mössbauer effect in polymers and in amorphous bodies. It appeared that, because of the optical vibration branches, recoilless gamma resonance occurs clearly in systems consisting mainly of light atoms: H, C, N, O. In addition it was shown to be possible to fix the extent of influence of the nearest neighbors of the Mössbauer atom, tin, and of the more distant chemical bonds. Finally, the asymmetric doublet structure in the quadrupole splitting of spectra from polycrystalline samples was investigated and explained. The results of these early
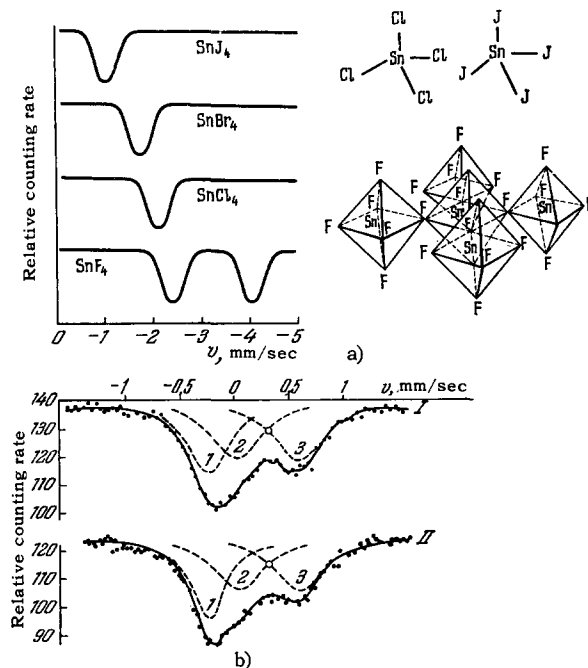

FIG. 10. Chemical gamma resonance spectroscopy. a) NGR spectra of tin halogens and their structures; [41]
$SnF_4 - \Delta \approx 1.7$ mm/sec, $K_2SnF_6 - \Delta = 0$; b) NGR spectra of cyanide complexes of iron—Prussian blue and Turnbull's blue, and the formulas for these compounds: [44] I—Prussian blue, $Fe(III) + [Fe(CN)_6]^{4-}$; II—Turnbull's blue, $Fe(II) + [Fe(CN)_6]^{3-}$: 1-singlet $[Fe(CN)_6]^{4-}$; 2,3-doublet Fe(III). Prussian blue ≡ Turnbull's blue: $[Fe(III)]_x[Fe(II)(CN)_6]_y$.

KI^{129}Cl$_4$·H$_2$O $\xrightarrow{\beta^-}$ XeCl$_4$,

KI^{129}O$_3$ $\xrightarrow{\beta^-}$ XeO$_3$,

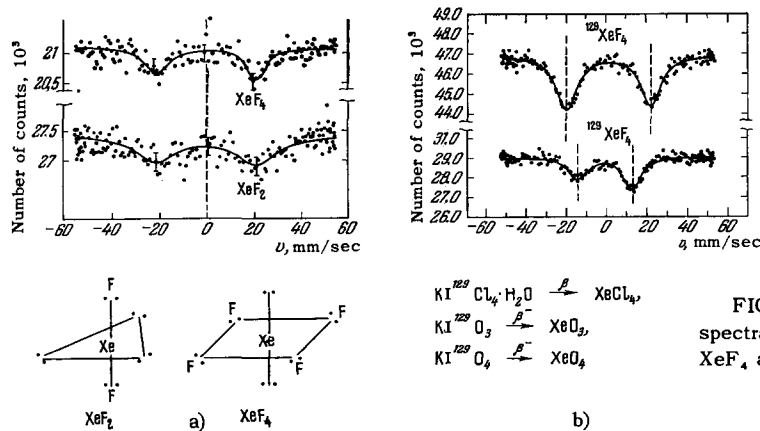KI^{129}O$_4$ $\xrightarrow{\beta^-}$ XeO$_4$

FIG. 11. Chemical gamma resonance spectroscopy. [48,49] a) NGR spectra of XeF$_2$ and XeF$_4$ and their structures; b) NGR spectra of XeF$_4$ and XeCl$_4$ resulting from β decay of KI^{129}Cl$_4$.

investigations of chemical gamma resonance spectro-
scopy were summarized in our monograph,[4,5] mate-
rial from which, along with later publications, we are
using here as examples.

Applications of nuclear gamma resonance to struc-
tural chemistry are illustrated in Figs. 10 and 11. The
marked difference of the spectrum of SnF_4 from the
spectra of other tin halogens (Fig. 10a) and analysis
of data on the chemical shift, quadrupole splitting, and
Mössbauer probability, enabled one to conclude that
the structure of SnF_4 is octahedral, that the tin has
coordination number six, and that its bonds with the
four bridging fluorine atoms, in the plane that results
in the formation of a peculiar inorganic polymer, are
different from the bonds to the two vertex atoms of
fluorine. It is interesting that in salts like K_2SnF_6 all
six Sn—F bonds are equivalent and the quadrupole
splitting of the lines disappears. Coordination num-
bers of 5 and 6 for tin were established by us for many
other tin-organic compounds.

Figure 10b shows the spectra of two complex com-
pounds of iron that have been known to chemists from
their student days—Prussian blue and Turnbull's blue.
In various laboratories abroad[42-46] and here (cf.[5])
it was shown that their spectra are identical; in most
of the papers cited (except for[46]) these spectra were
regarded as the superposition of a doublet from ions of
trivalent iron and a single line from a complex anion
of divalent iron—ferrocyanide $[Fe(CN)_6]^{4-}$. Thus, it
appeared that Prussian blue and Turnbull's blue are
one and the same compound, though obtained in differ-
ent ways, and it is now assumed that for both methods
of preparation, independent of whether the central atom
of the initial cyanide complex is di- or trivalent iron,
the iron inside the complex is in the Fe(II) state, while
in the outer coordination sphere it is in the Fe(III)
state.

The NGR spectra obtained at the Argonne National
Laboratory (USA) for xenon (Xe^{129} and Xe^{131}) in two
compounds of this "formerly inert" gas with fluo-
rine[47-49] enable one to establish the electronic struc-
tures of XeF_2 and XeF_4 shown in Fig. 11a. To these
two structures there should correspond quadrupole
splittings that are equal in magnitude (as is shown by
the experiment) but opposite in sign. Moreover, by
using as radiator the resonance gamma radiation from
a compound of radioactive iodine $KI^{129}Cl_4$ they were
able to show that in the β^- decay of the iodine (which
is transformed into the xenon isotope Xe^{129}) a previ-
ously unknown compound $XeCl_4$ is formed, which is
identified through its gamma resonance spectrum,
which is similar to that of XeF_4 (Fig. 11b). Similarly
the β^- decays of $KI^{129}O_3$ and $KI^{129}O_4$ lead to the for-
mation of the oxides of xenon XeO_3 and XeO_4. In these
measurements the Mössbauer effect was thus applied
simultaneously to important problems of chemical
structure and to the study of the chemical conse-
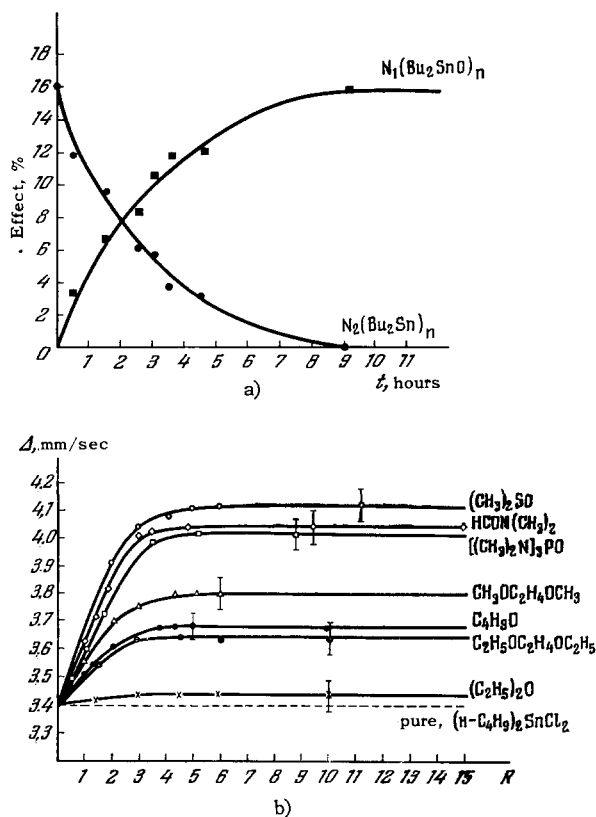quences of nuclear transformations, in this case, the
β^- decay of iodine.

FIG. 12. Chemical gamma resonance spectroscopy. a) Kinetic
curves, obtained from NGR spectra of tin, showing decrease in con-
tent of dibutyl tin $(Bu_2Sn)_n$ and increase in content of its oxidation
product dibutyl tin oxide $(Bu_2SnO_2)_n$;[50] b) increase in quadrupole
splitting of NGR spectral line of tin in dibutyl tin dichloride on
solution in different dipolar aprotonic solvents (R is the molar
ratio of concentrations of solvent and solute).[51]

Applications of gamma resonance spectroscopy to
chemical kinetics and the physical chemistry of sur-
face phenomena are illustrated in Figs. 12 and 13 with
several examples from work at the ICP. In Fig. 12a
we show the results obtained by observing, via the
changes with time of the intensity of NGR spectra of
initial materials and products, the kinetic curves for
oxidation in air of solid dibutyl tin with formation of
dibutyl tin oxide.[50] These reactions are accompanied
by a change in the valence bonds of the tin, i.e., the tin
Mössbauer atoms here participate in the chemical
transformation.

Of much more general interest is the following ex-
ample, where the atoms of tin served only as "ob-
servers," characterizing the properties of dipolar
aprotonic solvents.[51] Such solvents, as dimethyl-
formamide or tetrahydrofuran, are widely used in
organic chemistry and have a great influence on the
kinetics of nucleophilic heterolytic reactions. It ap-
pears that the properties of solvents can be quantita-
tively characterized by the increase in the quadrupole
splitting of the NGR spectra of polar compounds such
as dibutyl tin dichloride on solution (cf. Fig. 12b). In
fact, both the growth of the quadrupole splitting and the

kinetic effects have the same cause, the strong inter-
action of the solvent only with the cation, and not with
the anion part of the molecule. As a result the anions
which are detached from the cations and weakly sol-
vated are extremely reactive.

NGR spectra give information both about the chem-
ical state (chemical shifts, quadrupole splitting) and
about the dynamics of surface atoms (asymmetry of
quadrupole splitting). Thus, for example, observation
of spectra of tin on the surface of silica gel[52] showed
the presence of two oxides of the form SnO and SnO_2,
so that on the basis of the much higher temperature
dependence of the Mössbauer probability f' for the
adsorbed SnO_2 (Fig. 13a) one could conclude that the
oxide SnO is chemisorbed, whereas the dioxide SnO_2
is bound to the surface only by van der Waals forces.
From data on the asymmetry of the quadrupole split-
ting for SnO they were able to establish the mean
square amplitude of the thermal vibrations along the
surface (0.07 Å) and normal to it (0.13 Å); for SnO_2
they separated the effects on the Mössbauer probabil-
ity of the vibrations of the atoms in the molecule and
the vibrations of the molecules on the surface.

In the ICP there were obtained the first NGR spec-

tra[53] of synthetic zeolites, molecular sieves that
have attracted wide interest recently as effective sep-
arators and desiccators of mixtures. The structures
and absorbing properties of two types of zeolites were
investigated—faujasite (Y) and mordenite (M), with
cation displacement of sodium by iron highly enriched
in Fe^{57}. The basic structure of the unit cell of these
zeolites is a cubic octahedron, consisting of Si—O and
Al—O tetrahedra. The cubic octahedra, joined to one
another, form channels which provide the interior sur-
face of the zeolites. The spectra shown in Fig. 13b
enabled us to confirm directly the proposal recently
made by M. M. Dubinin that there are two types of
adsorption centers in zeolites—localized and unlocal-
ized. It appeared that before adsorption only the Fe(III)
ions are localized, whereas localization of Fe(II) is
achieved only as the result of filling up the channels
in the zeolite with various adsorbable materials
(hexane, for example). Correspondingly, before ad-
sorption one observes only the doublet structure of
trivalent iron, while after adsorption one gets in ad-
dition the doublet spectrum of Fe(II) with a very much
greater quadrupole splitting.

There is no question that there is a whole variety of
possibilities of using the NGR method in the physical
chemistry of polymers. A few examples are given in
Figs. 14 and 15.

Figure 14a shows the spectrum of tin in polymethyl
methacrylate, in which part of the methyl groups are
replaced by tin triethyl radicals; this is the first
Mössbauer spectrum of a polymer, obtained in 1961
in our work in collaboration with NPRI.[54]

A detailed investigation[55] was made of polymers
of ferrocene—the sandwich-shaped iron dicyclopenta-
dienyl, $Fe(C_5H_5)_2$. A comparison was made of spectra
of soluble and insoluble polyferrocenes, i.e., linear
polymers in whose chain only one of the two (C_5H_5)
rings from each iron atom participates, and polymers
with linked parts, in which both cyclopentadienyl rings
give polymer bonds, and we get a solid net where the
atoms of iron alternate with organic rings in a typical
conjugated system. The spectrum of such an insoluble
polymer (Fig. 14b) consists of two doublets, where the
linked sections give the smaller quadrupole splitting
and relatively greater Mössbauer probability—at room
temperature, gamma resonance is seen only for these
parts. Such changes in the spectra enable one to deter-
mine directly the degree of cross-linking of the poly-
ferrocene, and also show the raising of electrons into
collective conduction levels in the linked parts—a fact
that is extremely important for the description of the
properties of organic semiconductors.

Extremely interesting results were obtained in joint
work with the NPRI of Moscow State University, the
Scientific Institute of the Cable Industry (NIIKP) and the
L. Ya. Karpov Physico-chemical Institute (NIFKhI)[56]
in studying radiation effects on polyethylene containing
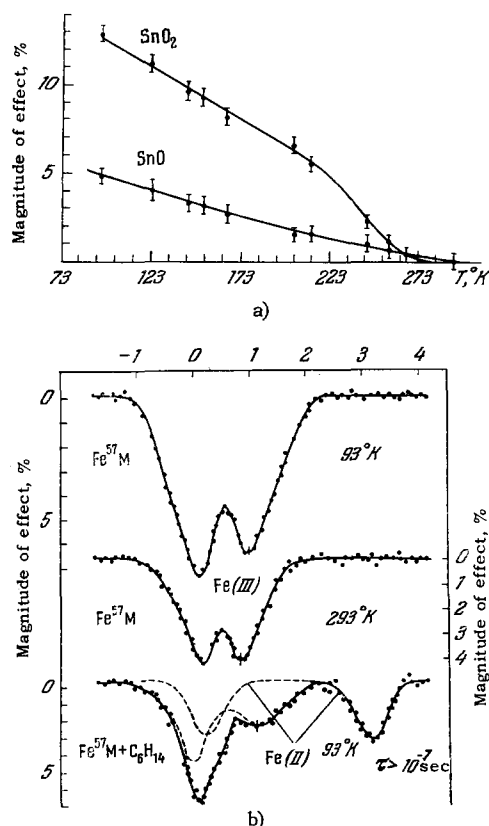additives of the stabilizer tin dibutyl dimaleate. The

FIG. 13. Chemical gamma resonance spectroscopy. a) Tem-
perature dependence of Mössbauer probability f' for two oxides
of tin absorbed on silica gel: SnO and SnO_2;[52] b) spectrum of
of iron in zeolite M (mordenite) before absorption (at 93 and
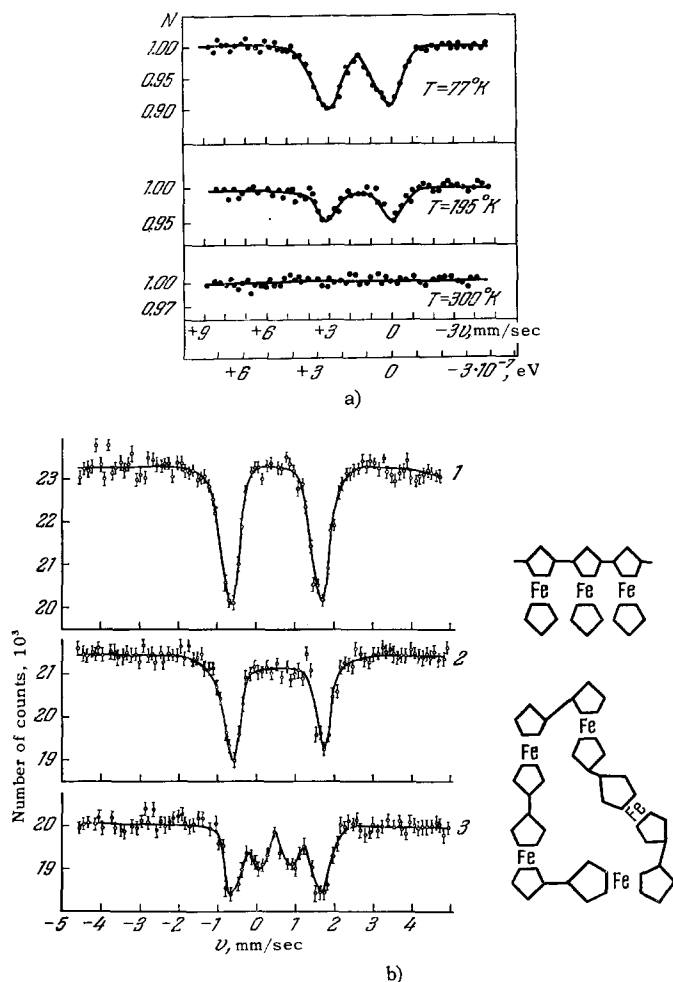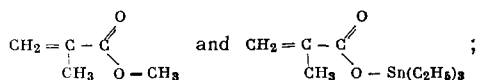293°K) and after absorption of hexane (93°K).

FIG. 14. Chemical gamma resonance spectroscopy. a) First NGR spectrum of a polymer (polymethyl methacrylate with tin triethyl introduced in side chains)[54]

$$CH_2 = C - C \overset{O}{\underset{CH_3 \quad O - CH_3}{\diagdown}} \quad \text{and} \quad CH_2 = C - C \overset{O}{\underset{CH_3 \quad O - Sn(C_2H_5)_3}{\diagdown}} ;$$

b) NGR spectra and schematic structures of ferrocene (1), soluble (2) and insoluble (3) polyferrocene.[55]

marked change of the chemical shift of the tin in the NGR spectra of these materials on irradiation (Fig. 15a) shows the unchaining of the two butyl radicals with conversion of tetravalent tin to divalent. Apparently this is also the way that tin organic additives act as inhibitors of oxidation aging of polymers.

In a series of investigations of kinetics of chemical transformations, in particular in the work of V. A. Kargin and his group, who studied solid phase polymerization, it was shown that there is a marked speedup of reactions in the neighborhood of the melting point or near phase transitions in the solid state. Such a speedup apparently was related to an increase in mobility in the solid phase. Of particular interest in this connection are the data of Hungarian workers[57] on the temperature dependence of the Mössbauer probability in various iron salts in ice. As we see from Fig. 15b, in
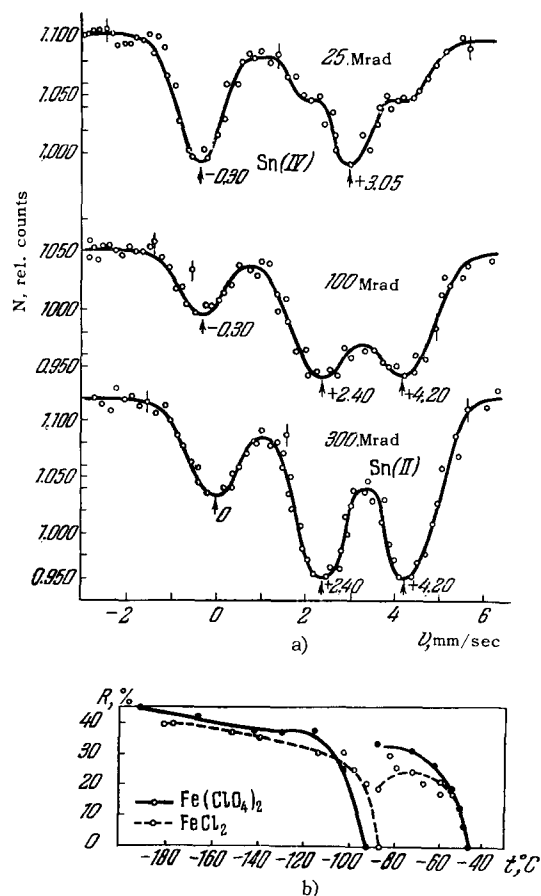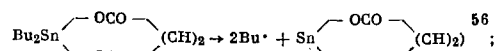

FIG. 15. Chemical gamma resonance spectroscopy. a) NGR spectra of tin dibutyl dimaleate, embedded in polyethylene, before and after irradiation with a Co^{60} γ source (decomposition

$$Bu_2Sn \overset{OCO}{\underset{OCO}{\diagup}} (CH)_2 \rightarrow 2Bu \cdot + Sn \overset{OCO}{\underset{OCO}{\diagup}} (CH)_2 ;$$

b) temperature dependence of Mössbauer probability f' for iron in frozen aqueous solutions of $Fe(ClO_4)_2$ and $FeCl_2$ near the point of phase transition of ice.[57]

a certain region of temperatures around $-90°C$, the recoilless nuclear gamma resonance for iron atoms in $Fe(ClO_4)_2$ and $FeCl_2$ simply disappears, which directly demonstrates a marked increase in the mobility of the iron atoms in the ice near the phase transition point. This result is very similar to that obtained later (but for transitions of the second kind) in studying ferroelectrics, which we mentioned earlier.

VI. NUCLEAR GAMMA RESONANCE AS A METHOD OF PHYSICO-CHEMICAL ANALYSIS

Now let us consider various analytic applications of gamma resonance spectroscopy.

First I should like briefly to remind you of one special but very promising possibility of using the Mössbauer effect as an analyzer, using tracer methods.[58,59] Since gamma resonance is observed only for particular isotopes of an element (for example,
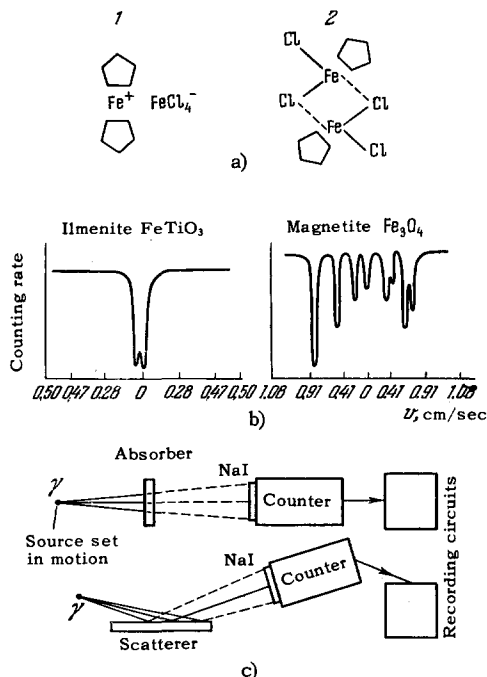
FIG. 16. Analytical applications of gamma resonance spectroscopy. a) Mössbauer effect as analyzer in tracer method—and choice between two structures for ferricene-ferrichloride; [59] b) NGR spectra of two iron minerals—ilmenite and magnetite; [60] c) principle of operation of gamma resonance tin detector using absorption and scattering of resonance γ quanta.

Fe[57]), we have a new way of studying the kinetics and reaction mechanisms of complex reactions or the structures of many chemical compounds. To do this we study the dependence of the form of the NGR spectrum on the particular chemical state in which the Mössbauer isotope is introduced into the system; for example, we see the effect on the spectrum of a system containing iron in both divalent and trivalent states when we enrich only one or the other state with Fe[57]. The very first attempts at combining the Mössbauer effect with tracer methods led to the discovery of electron exchange between Fe(II) and Fe(III) ions in solid salts at 78°K [58] and enabled a choice between the two different structures shown in Fig. 16a for ferricene-ferrichloride $Fe(C_5H_5)_2FeCl_4$, in favor of the first. [59]

Even more extensive, of course, are the possibilities of using the Mössbauer effect in pure form (without tracer atoms). Recoilless nuclear gamma resonance is an extremely powerful tool for analysis. Of especial importance is the fact that, unlike the technique of activation analysis, which is also a product of nuclear physics, the NGR method enables us not only to detect the presence of a particular element in a system, but also to establish its chemical state.

As an example, in Fig. 16b we show the Mössbauer spectra of two iron minerals—ilmenite ($FeTiO_3$) and magnetite (Fe_3O_4), taken from joint work of the Institute for Nuclear Geology and Geophysics of the Min-

istry for Geology of the USSR, JINR, and ICP. [60] The spectra were taken at room temperature, where a magnetic splitting was seen for magnetite but none for ilmenite. Thus, without chemical procedures and even remotely, one can by scattering the γ quanta from the source off the surface under investigation, distinguish these two minerals and solve various other similar problems. The ratio of ilmenite to magnetite in the ore determines such a question as its suitability for iron ore (Fe/Ti > 10) or titanium ore (Fe/Ti < 10).

There are statements in the literature [61,62] that propose applying the Mössbauer effect for remote analysis (from a space vehicle) of the mineral content of the surfaces of the Moon and of Mars.

I am pleased to report to the General meeting of the USSR Academy of Sciences that we have had definite successes in practical uses of the analytical possibilities of the NGR method.

Starting in 1962, two groups of scientists independently developed designs of gamma resonance instruments for analysis of ores and minerals for their content of tin in the form of cassiterite (SnO). The first of these groups included people from our laboratory at the ICP, from the State institute for Instrumentation (SNIIP), the USSR State Atomic Energy Committee, and the Institute for Nuclear Geology and Geophysics; the second, workers from NPRI and the Institute for Petroleum Synthesis (INKhS) of the USSR Academy of Sciences. During 1963-65, both groups successfully tested such equipment under field conditions on various deposits of tin. The instrument of our group, using only standard parts, was accepted in the summer of 1965 by the interdepartmental commission and put into mass production. The principle of its operation in both absorption and scattering of γ quanta by the specimens under investigation is shown in Fig. 16b. Instead of getting ores in the laboratory and using rather complicated chemical procedures, it is sufficient to verify whether the counting rate for γ quanta depends on whether the resonant source is at rest or moving noticeably. Within a few minutes the tin content of rocks (for concentrations of 0.05—4%) is determined to an accuracy no worse than that required of chemical analysis. A photo of the portable γ resonance tin-seeker MAK-1 (total weight about 3.5 kg) is shown in Fig. 17 (the two arrangements of the geometry, a) and b), correspond to using the apparatus in absorption or scattering). From the estimates of geologists and economists each such instrument (several hundred have already been ordered) will give a yearly saving of more than 7,000 rubles. Requests have been received from abroad for licensing the production or sale of instruments made according to information from the Russian authors.

The Research Institute for Instrumentation of the State Commission on Atomic energy together with ICP also has developed models of instruments for deep logging of tin-containing rocks (Fig. 18a) for the con-
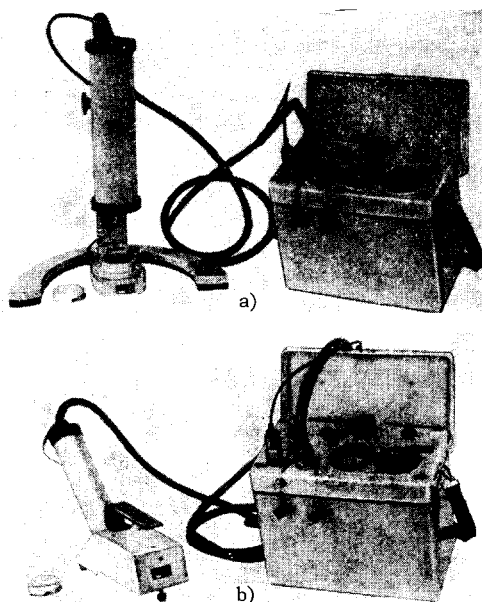
FIG. 17. External view of γ resonance tin-seeker MAK-1 arranged to work using a) absorption and b) scattering.

trol of composition of pulps in enrichment processes (Fig. 18b) and a typical γ resonance spectrometer for laboratory studies (Fig. 19).

In connection with the great interest now being devoted by the Presidium of the USSR Academy of Sciences to instrumentation, one should particularly emphasize the importance of the work done by the State Research Institute for Instrumentation and the need to support it in every way.

VII. SOME BIOLOGICAL APPLICATIONS OF THE NGR METHOD

The application of the Mössbauer effect to biology is favored at present mainly because one of the principal elements showing the effect is iron. Iron enters
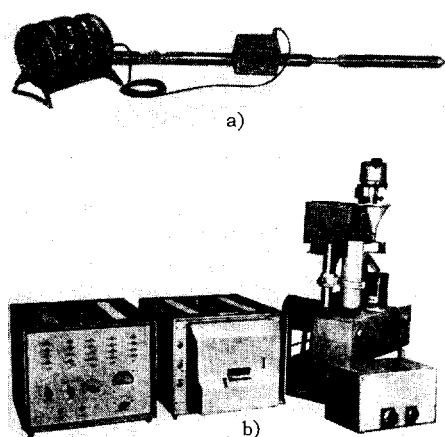

FIG. 18. External view of γ resonance instrument for deep logging a) and control of composition of pulp in enrichment processes b).
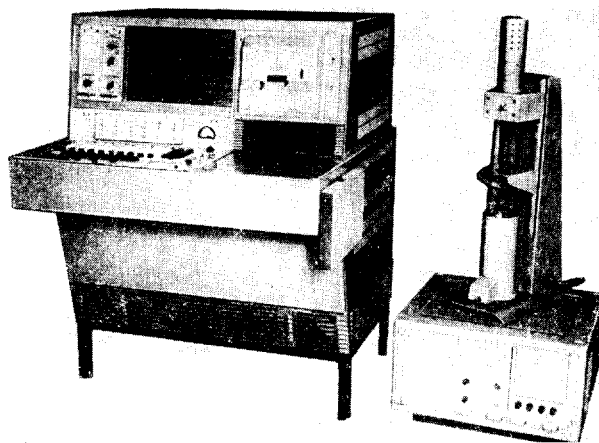

FIG. 19. External appearance of typical laboratory γ resonance spectrometer.

into the constituents of hemoglobin and many enzymes, is present in all nucleic acids, and seems to play a significant, but as yet not understood, biological role. In this regard it is enough to cite one very interesting fact. The tobacco mosaic virus contains at most hundredths of a percent of iron. But removing this negligible amount of iron deprives the virus of its infectious properties and leads to breakup of the RNA molecule into finer subunits, as shown by sedimentation measurements. Conversely, adding iron revives the RNA and establishes the infectious properties of the virus.[63] Before one could explain the reason for the biological role of iron, one naturally had to establish the nature of its chemical binding in nucleic acids, which was unknown until recent γ spectroscopic studies done by us at ICP.[64,65] From a comparison of the spectra of $FeCl_3$ and its complexes with nitrogeneous bases—guanine and guanosine, with sugars—ribose and desoxyribose, and with the nucleic acids RNA and DNA (Fig. 20), it was shown that inclusion of iron in the composition of RNA and DNA is achieved mainly by the formation of coordination bondings of Fe(III) ions with sugar, which plays the role of an active electron donor in RNA (ribose), reducing the iron to Fe(II), but does not show donor properties in DNA. It is possible that these data may shed some light on the important question of the reason for the essential difference in the biological roles of RNA and DNA. The main difference between these acids (aside from the replacement of one of the nitrogeneous bases—thymine-DNA, by uracil-RNA) is the change in structure of the sugar, whose active chemical and biological role had not been suspected before this.

Figure 21b shows the first NGR spectrum of a living object—the hydrogenous bacteria Hydrogenomonas-Z-1, fed with trivalent iron enriched in Fe^{57}. These data were obtained at the ICP.[66] One sees in the spectrum components due to each of the fundamental valence states of the iron, Fe(II) and Fe(III), apparently entering in the cytochromic system of these bacteria.
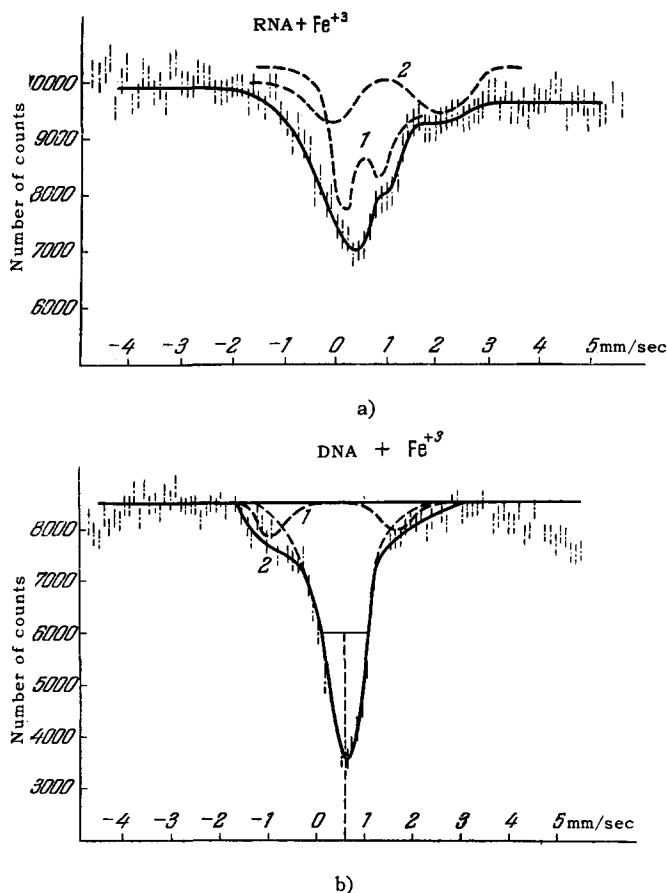
FIG. 20. Gamma resonance spectroscopy in biology. NGR spectra of iron bound to RNA (a) and DNA (b). In the case of RNA the complexity of the spectrum is caused by the presence of two valence states of the iron—Fe(III)(1) and Fe(II)(2); in the case of DNA the spectrum is a superposition of a singlet from a complex of Fe(III) with guanine and a doublet from a tetragonal high-spin complex of Fe(III).

An interesting problem for future experiments is the study of the metabolism of iron in organisms by using the NGR method.

Rather more work has been done on the Mössbauer effect for iron in hemin and hemoglobin. The spectrum of hemin, obtained at the ICP on a high resolution NGR spectrometer is shown in Fig. 21. The complex structure of this spectrum has still not been discussed satisfactorily, and there is great interest in a check of the statement of American workers [67] that there is magnetic hfs in the NGR spectrum of hemin.

The biological applications of the NGR method are not limited to problems of biochemistry. For example, an interesting investigation in biomechanics was done in Israel. [68] Sound vibrations produced a motion of the ear drum to which a miniature source of resonant γ quanta—Co⁵⁷, was attached (the absorber was Fe⁵⁷). Since the vibration frequency was set $(10^3-10^4 \text{ sec}^{-1})$ and the velocities (of order 10^{-4} cm/ sec) determined from the Doppler shift of the absorption maximum in the NGR spectrum, one could thus
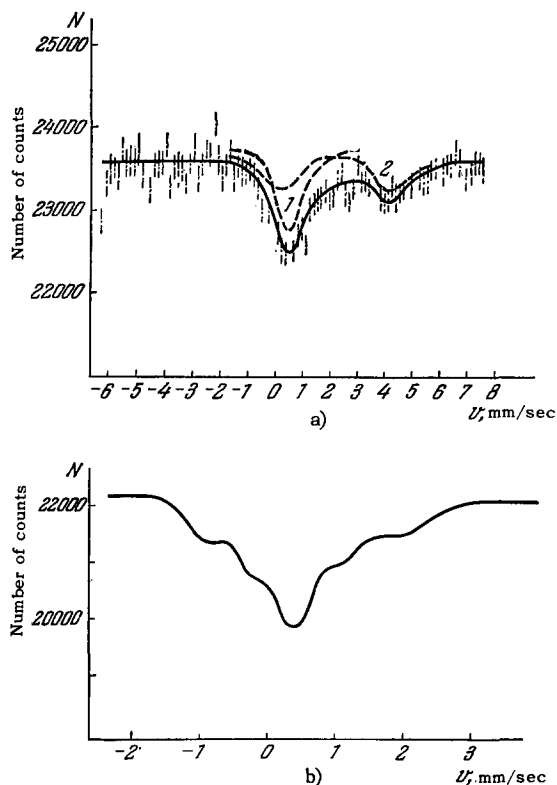

FIG. 21. Gamma resonance spectroscopy in biology. a) NGR spectrum of iron in hydrogenous bacteria Hydrogenomonas-1, grown in a medium with trivalent Fe⁵⁷. The complexity of the spectrum is caused by the presence of the two valence states of the iron, Fe(III) and Fe(II); b) NGR spectrum of iron in hemin (commercial sample from "Light Co."). The complexity of the spectrum is assumed to be related to the presence of magnetic hfs.

directly measure the vibration amplitudes, which were a few Å ($1 \text{ Å} = 10^{-8}$ cm—of the size of atoms!!) to an accuracy of $1-2$ Å.

VIII. EXAMPLES OF ENGINEERING APPLICATIONS OF THE NGR METHOD

The example from biomechanics is a very close analog of a variety of engineering applications of the Mössbauer effect for all sorts of measurements—of velocities, shifts, accelerations, etc, for control of various quantities and for adjusting them. The theoretical basis for such applications, the principles for producing various schemes, and ways of optimizing their parameters have been successfully developed in the Institute for Automation and Telemechanics [69-72] under the general direction of B. N. Petrov and N. N. Shumilovskiĭ. Several variants of engineering applications of the Mössbauer effect were recently presented in a survey paper printed in "Zavodskaya Laboratoriya". [73] Here we shall only indicate some of the main schemes. A practically complete analog of the biomechanical experiment is the recording (in particular, without contacts) of all kinds of vibrations of machine parts and mechanisms. In this case the quan-

tity directly determined is the product of the vibration frequency and its amplitude. At a frequency of 10 Mz one can detect a vibration with an amplitude of 1 micron. The weight of the equipment is several kilograms, the time needed is of the order of minutes.

The influence of the Doppler shift on the conditions for nuclear resonance is the main way of measuring the relative velocity of two objects, as shown in Fig. 22a. By using the Mössbauer effect one can measure, and by means of feedback one can also control, velocities between a few microns and tens of meters per second. There are mentions[61] in the literature of a possible use of nuclear γ resonance for controlled approach and docking of space ships, for soft landings on the Moon and planets without atmospheres. A natural application of the NGR method is the determination of velocities of coastal shifts, velocities of flow of rivers and oceans, etc.

A slight modification of these schemes enables one to measure accelerations (we recall the work of Pound and Rebka, where the parameters included the acceleration in the gravity field of the Earth); there are proposals[61] for using the Mössbauer effect for determination of the initial acceleration of a rocket on takeoff. One can also measure the velocity of rotation in isolated systems (Fig. 22b); in the absence of vibration, in a system with radium 1 m one can record rotation velocities to an accuracy of 0.2 rps.

By using a generator of standard frequency pulses and a scheme for comparing these pulses with the indications from a γ ray detector, one can detect and measure minute displacements of various objects in a closed region. If, for example, the velocity of such a displacement does not exceed ~ 1 mm/sec, one can fix its value within 1μ to 1 mm over the whole path of the body (cf. Fig. 22c).

Figure 22d shows a schematic of an arrangement for measuring high pressures, applicable with slight changes to the study of deformations and stresses in solids. Here the pressure measurements can be based on the dependence of either the chemical shifts or the Mössbauer probability on the compression of the material.

Finally, we recall that one can make measurements of low temperatures, based on the changes in polulations of hfs components in NGR spectra, when kT becomes comparable with the energy differences of individual lines in the hfs: $kT \lesssim 10^{-5}$ eV, i.e., $T \lesssim 0.1°K$ (Fig. 22e).

Really, it is difficult to give another example of a phenomenon with such universal application as recoilless nuclear γ resonance!

In a recent paper of the president of the Academy of Sciences of the USSR, M. V. Keldysh, "Science and Technical Progress" ("Pravda," Oct. 10, 1965), it is stated that: "It is extremely important that problems of realizing the achievements of science be posed in good time for industry... In doing this we must make
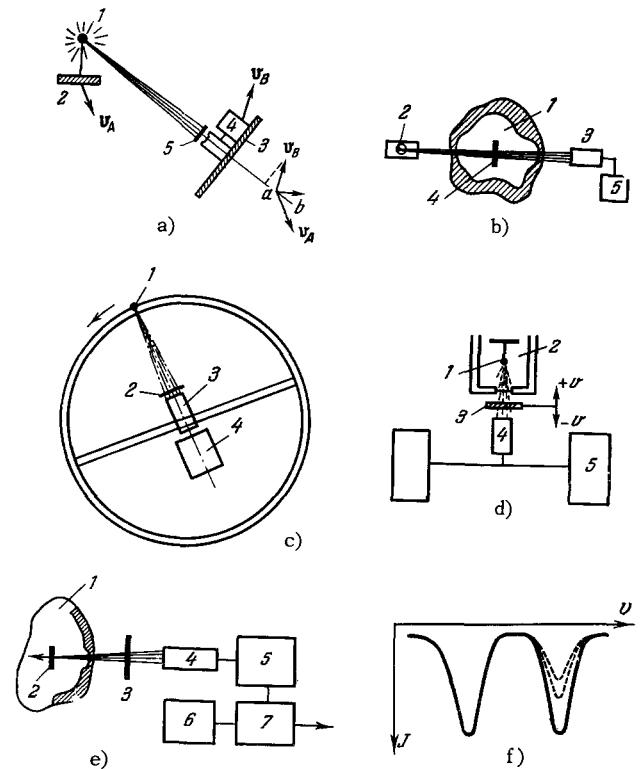

FIG. 22. Schematic diagrams of some engineering applications of the NGR method. a) Schematic of arrangement for determining the relative velocity of two objects: 1—source of quanta, 2—object A, 3—object B, 4—electronic circuit, 5—absorber; b) schematic of method for recording rate of rotation of an isolated system: 1—source of γ radiation, 2—absorber, 3—counter, 4—recording equipment; c) schematic of arrangement for measuring small movements of parts in an enclosed region: 1—closed region, 2—moving part, 3—absorber, 4—counter, 5—counting circuit, 6—pulse generator, 7—comparison circuit; d) schematic of method for measuring high pressures: 1—volume in which pressure is produced, 2—source of γ radiation, 3—counter, 4—absorber, 5—electronic circuit; e) schematic of equipment for measuring low temperatures: 1—source of γ radiation, 2—volume at low temperature, 3—moving absorber, 4—counter, 5—electronic equipment (the nature of the change in occupation of levels is shown in f) for the region $T < 1°K$).

use not only of our own achievements, but also those of world science and technology." The Mössbauer effect is undoubtedly one that has many directions for its development. One important point should be emphasized. In the past, it has happened frequently that discoveries of Russian scientists have not found application in our country, but have come back to us years later from other lands. Now the situation has changed fundamentally. This is shown not only in the significant and rapidly made discoveries of our compatriots, but also, for example, by the still brief history of recoilless nuclear gamma ray spectroscopy. Although the honor for its discovery belongs to a foreign scientist, the importance of the discovery for a variety of branches of science and technology was understood, established and demonstrated by us. The theoretical work of our scientists in this field, Soviet experimental

studies in nuclear physics and solid state physics, our establishment and development of chemical γ resonance spectroscopy, the interesting biological results obtained using NGR—, all of these have received international recognition, and are regarded as very important contributions both to the development of γ resonance spectroscopy, and to the various branches of science.

At the end of the past year the Presidium of the Academy of Sciences of the USSR accepted an extensive directive concerning the development of work on nuclear gamma resonance, pointing out the main problems for future study and steps for accomplishing them. It would be very desirable if our physicists, chemists, biologists, geologists, engineers and instrument makers thought about and discussed the entirely new ways of investigation opened up by gamma resonance spectroscopy. A close cooperation of specialists in all areas is the essential guarantee of success in developing and applying this important method.

Note added in proof. We should point out that in a paper just published (A. A. Komissarova, A. A. Sorokin and V. S. Shpinel', JETP 50, 1206 (1966), Soviet Phys. JETP 23, 800 (1966), Shpinel' and his coworkers have retracted their erroneous work [19] (which is not even cited in their new paper) and agree completely, both in general and also for the specific case of tin-organic compounds, with the explanation given on p. 00 of the integral asymmetry of the quadrupole splitting of gamma resonance spectra, [16,17,18] which applies to spectra both from absorption and scattering.

[1] R. L. Mössbauer, Z. Physik 151, 124 (1958).

[2] R. L. Mössbauer, Naturwiss. 45, 538 (1958).

[3] R. L. Mössbauer, Z. Naturforsch. 14a, 211 (1959).

[4] V. I. Gol'danskiĭ, Effekt Mёssbauera i ego primeneniya v khimii, Moccow, Press of the Academy of Sciences, USSR, 1963.

[5] V. I. Goldanskiĭ, The Mössbauer Effect and Its Applications in Chemistry, Consultants Bureau, New York, 1964 (translation of preceding reference, with supplement).

[6] Yu. M. Kagan, JETP 41, 659 (1961), Soviet Phys. JETP 14, 472 (1962).

[6a] Yu. M. Kagan and V. A. Maslov, JETP 41, 1296 (1961), Soviet Phys. JETP 14, 922 (1962).

[7] Yu. M. Kagan and Ya. A. Iosilevskiĭ, JETP 42, 259 (1962), Soviet Phys. JETP 15, 182 (1962).

[7a] Yu. M. Kagan and Ya. A. Iosilevskiĭ, JETP 44, 284 (1963), Soviet Phys. JETP 17, 195 (1963).

[8] Yu. M. Kagan, DAN, SSSR 140, 794 (1961), Soviet Phys. Doklady 6, 881 (1962).

[9] N. E. Alekseevskiĭ, Pham Zuy Hien, V. G. Shapiro, and V. S. Shpinel', JETP 43, 790 (1962), Soviet Phys. JETP 16, 559 (1963).

[10] M. I. Podgoretskiĭ and A. V. Stepanov, JETP 40, 561 (1961), Soviet Phys. JETP 13, 393 (1961).

[11] M. A. Krivoglaz, JETP 40, 1812 (1961), Soviet Phys. JETP 13, 1273 (1961).

[12] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).

[13] V. A. Belyakov, Phys. Letters 16, 279 (1965).

[14] V. I. Goldanskiĭ and E. F. Makarov, Phys. Letters 14, 111 (1964).

[15] I. V. Bersuker, V. I. Gol'danskiĭ, and E. F. Makarov, JETP 49, 699 (1965), Soviet Phys. JETP 22, 485 (1966).

[16] V. I. Gol'danskiĭ, G. M. Gorodinskiĭ, S. V. Karyagin, L. A. Korytko, E. F. Makarov, I. P. Suzdalev, and V. V. Khrapov, DAN 147, 127 (1962).

[17] V. I. Gol'danskiĭ, E. F. Makarov, and V. V. Khrapov, JETP 44, 752 (1963), Soviet Phys. JETP 17, 508 (1963).

[18] S. V. Karyagin, DAN 148, 1102 (1963).

[19] Shpinel', Aleksandrov, Ryasnyi and Okhlobystin, JETP 48, 69 (1965), Soviet Phys. JETP 21, 47 (1965).

[20] M. Blume, Phys. Rev. Letters 14, 96 (1965).

[21] A. M. Afanas'ev and Yu. M. Kagan, JETP 45, 1660 (1963), Soviet Phys. JETP 18, 1139 (1964).

[21a] Yu. M. Kagan and A. M. Afanas'ev, JETP 47, 1108 (1964), Soviet Phys. JETP 20, 743 (1965).

[22] A. M. Afanas'ev and Yu. M. Kagan, JETP 48, 327 (1965), Soviet Phys. JETP 21, 215 (1965).

[22a] Yu. M. Kagan and A. M. Afanas'ev, JETP 50, 271 (1966), Soviet Phys. JETP 23, 178 (1966).

[23] Yu. M. Kagan and A. M. Afanas'ev, JETP Letters 2, 130 (1965), translation p. 81.

[24] M. I. Podgoretskiĭ and I. I. Roĭzen, JETP 39, 1473 (1960), Soviet Phys. JETP 12, 1023 (1961).

[25] V. A. Bryukhanov, N. N. Delyagin, and V. S. Shpinel', JETP 42, 1183 (1962), Soviet Phys. JETP 15, 820 (1962).

[26] G. E. Bizina, A. G. Beda, N. A. Burgov, and A. V. Davydov, JETP 45, 1408 (1963), Soviet Phys. JETP 18, 973 (1964).

[27] R. V. Pound and G. A. Rebka, Phys. Rev. Letters 4, 274 (1960).

[28] R. V. Pound, UFN 72, 673 (1960), Soviet Phys. Uspekhi 3, 875 (1961).

[29] I. Ya. Barit, M. I. Podgoretskiĭ, and F. L. Shapiro, JETP 38, 301 (1960), Soviet Phys. JETP 11, 218 (1960).

[30] V. A. Bryukhanov, N. N. Delyagin, and Yu. M. Kagan, JETP 45, 1372 (1963), Soviet Phys. JETP 18, 945 (1964).

[31] I. I. Lukashevich, V. V. Sklyarevskiĭ, V. V. Samoĭlov, E. P. Stepanov, K. P. Aleshin, and N. I. Filippov, JETP Letters 3, 81 (1966), translation p. 50.

[32] V. I. Nikolaev, Yu. I. Shcherbina, and S. S. Yakimov, JETP 45, 1277 (1963), Soviet Phys. JETP 18, 878 (1964).

[33] I. Nowik and H. H. Wickman, Phys. Rev. A140, 869 (1965).

[34] V. I. Gol'danskii, V. F. Belov, M. N. Devisheva, and V. A. Trukhtanov, JETP 49, 1681 (1965), Soviet Phys. JETP 22, 1149 (1966).

[35] V. V. Sklyarevskiĭ, I. I. Lukashevich, V. N. Romanov, N. I. Filippov, Yu. N. Venevtsev, and N. S. Viskov, JETP Letters 3, 212 (1966), translation p. 135.

[36] R. J. Borg, R. Booth, and C. E. Violet, Phys. Rev. Letters 11, 464 (1963).

[37] P. P. Craig and W. W. Steyert, Phys. Rev. Letters 13, 802 (1964).

[38] M. B. Stearns and S. S. Wilson, Phys. Rev. Letters 13, 313 (1964).

[39] V. I. Gol'danskiĭ, V. A. Trukhtanov, M. N. Devisheva and V. F. Belov, JETP Letters 1, 31 (1965), translation p. 19.

[40] K. P. Belov and I. S. Lyubutin, JETP Letters 1, 26 (1965), translation p. 16.

[41] V. I. Gol'danskiĭ, E. F. Makarov, R. A. Stukan, T. N. Sumarokova, V. A. Trukhtanov, and V. V. Khrapov, DAN SSSR 156, 400 (1964).

[42] L. M. Epstein, J. Chem. Phys. 36, 2731 (1962).

[43] J. F. Duncana and P. W. R. Wrigley, J. Chem. Soc. 1120 (1963).

[44] W. Kerler, W. Neuwirth, E. Flück, P. Kuhn, and B. Zimmermann, Z. Physik 173, 321 (1963).

[45] E. Flück, Adv. Inorg. and Radiochem. 6, 433 (1964).

[46] K. Ono and A. Ito, Revs, Modern Phys. 36, 459 (1964).

[47] C. L. Chernick, C. E. Johnson, Y. G. Malon, G. J. Perlow, and M. R. Perlow, Phys. Letters 5, 103 (1963).

[48] G. J. Perlow and M. R. Perlow, Revs. Modern Phys. 36, 353 (1964).

[49] G. J. Perlow and M. R. Perlow, J. Chem. Phys. 41, 1157 (1964).

[50] V. I. Gol'danskiĭ, V. Ya. Rochev, and V. V. Khrapov, DAN SSSR 156, 909 (1964).

[51] V. I. Goldanskii, O. Yu. Okhlobystin, V. Ya. Rochev, and V. V. Khrapov, J. Organomet. Chem. 4, 160 (1965).

[52] I. P. Suzdalev, V. I. Gol'danskiĭ, E. F. Makarov, A. S. Plachinda, and L. A. Korytko, JETP 49, 1424 (1965), Soviet Phys. JETP 22, 979 (1966).

[53] V. I. Gol'danskiĭ, I. P. Suzdalev, A. S. Plachinda, and L. G. Shtyrkov, DAN SSSR 168, (1966).

[54] V. F. Bryukhanov, V. I. Gol'danskiĭ, N. N. Delyagin, E. F. Makarov, and V. S. Shpinel', JETP 42, 637 (1962), Soviet Phys. JETP 15, 443 (1962).

[55] V. F. Belov, T. P. Vishnyakova, V. I. Gol'danskiĭ, E. F. Makarov, Ya. M. Paushkin, T. A. Sokolinskaya, R. A. Stukan, and V. A. Trukhtanov, DAN SSSR 159, 831 (1964).

[56] A. Yu. Aleksandrov, S. M. Berlyant, V. L. Karpov, S. S. Leshchensko, O. Yu. Okhlobystin, É. É. Finkel', and V. S. Shpinel', Vysokomol. soed. 6, 2105 (1964).

[57] I. Dezsi, L. Keszthelyi, B. Molnar, and L. Pocs, Phys. Letters 18, 28 (1965).

[58] R. A. Stukan, V. I. Gol'danskiĭ, and E. F. Makarov, DAN SSSR 165, 1347 (1965).

[59] R. A. Stukan and L. P. Yur'ev, DAN SSSR 167, No. 6 (1966).

[60] V. I. Gol'danskiĭ, B. G. Egiazarov, V. M. Zaporozhets, Yu. M. Ostanevich, and I. S. Chuprova, Prikl. geofiz. 44, 202 (1965).

[61] P. J. Klass, Aviation Week and Space Technology, Sept. 9, 1963, p. 89.

[62] Angew. Chem. 77(13), 265 (1965).

[63] H. S. Loring, Y. Fujimoto, and L. F. Eng, Proc. Natl. Acad. Sci. USA 45, 287 (1959).

[64] R. A. Stukan, A. N. Il'ina, Yu. Sh. Moshkovskii, and V. I. Gol'danskiĭ, Biofizika 10, 343 (1965).

[65] Yu. Sh. Moshkovskiĭ, A. N. Il'ina, R. A. Stukan, and V. I. Gol'danskiĭ, Biofizika 11, 524 (1966).

[66] Yu. Sh. Moshkovskiĭ, E. F. Makarov, G. A. Zavarzin, I. Ya. Vedenina, S. S. Mardanyan, and V. I. Gol'-danskiĭ, Biofizika 11, 357 (1966).

[67] A. J. Bearden, T. H. Moss, W. S. Caughey, and C. A. Beaudreau, Proc. Nat. Acad. Sci. USA 53, 1246 (1965).

[68] P. Hillman, H. Schechter, and M. Rubinstein, Revs. Modern Phys. 36, 360 (1964).

[69] N. N. Shumilovskiĭ, V. S. Shpinel', D. Ya. Libenson, N. N. Delyagin, V. A. Bryukhanov, L. V. Mel'tser, K. P. Mitrofanov, Yu. V. Gushchin, and I. A. Braun, Disclosure No. 159386 dated October 21, 1962.

[70] N. N. Shumilovskiĭ, L. V. Mel'tser, and I. A. Braun, Izv. AN SSSR, Tekh. kibernetika 6, 111 (1963).

[71] I. A. Braun, Reports of the Third All-Union Congress on Automatic Control (Odessa, 1965).

[72] N. N. Shumilovskiĭ, N. Salakhutsinov, and A. A. Kalmakov, Izv. Akad. Nauk Ukr. SSR (ser. eng. sci.) 5, 29 (1964).

[73] V. I. Gol'danskii and E. F. Makarov, Zavodskaya laboratoriya 31, 61 (1965).

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