The Mössbauer effect

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A review is given of some nontrivial experiments in which the Mössbauer effect is applied, such as the measurement of the gravitational frequency shift of a γ quantum under terrestrial conditions, the search for an electric dipole moment of the photon, and the direct observation of the diffusion mechanism in solids. To obtain new results in experiments involving the measurement of extremely small energy shifts it is necessary to develop and significantly improve the Mössbauer technique using the isotope ^{67}Zn, which is the best in the energy resolution. A special role in the development of Mössbauer investigations in Dubna was played by F. L. Shapiro, who was one of the first in the USSR to understand the significance of the Mössbauer effect as a tool for solving fundamental physical problems.

I learned about the Mössbauer effect[1] in January 1960, in Dubna. A few days after I arrived in Dubna, where I was going to start working with polarized neutrons, Fedor L'vovich Shapiro told me to get acquainted with everything going on at the Laboratory of Neutron Physics. I eventually ran into Yuriĭ Ostanevich, who showed me the Mössbauer experiment. In the course of the conversation he happened to mention that owing to the thermal vibrations of the atoms the gamma emission (absorption) line is "shifted" and resonance absorption does not occur. I then asked, "And why aren't the nuclei frozen?" He answered, "Well, that's how Mössbauer proceeded," and pointed to the cryostat. Later in my ruminations I returned several times to this conversation, and I found it strange that without understanding the complete picture of this phenomenon, Mössbauer had followed the right track.... To be precise, in setting up his first experiment Mössbauer proceeded in quite the opposite way. He thought that the emission and absorption lines of ^{191}Ir were shifted by twice the nuclear recoil energy, but they are broadened owing to the thermal motion of the atoms, so that they slightly overlap. In order to decrease this overlap, i.e., to approach zero resonance scattering, Mössbauer decided to lower the temperature of the source and absorber, but instead of diminishing as expected, the resonance effect became stronger.

...And so I came to learn that intensive work had begun on the Mössbauer effect in Dubna. It turned out that in July and September of 1959 there had been seminars at which there was discussion of the appearance of a new resonance method which could be used to measure even the gravitational red shift under terrestrial conditions.

It is well known that at the beginning of this century Einstein predicted the gravitational red shift on the basis of the equivalence principle. Before this it had been experimentally demonstrated that there is a strict proportionality between the gravitational force with which a body is attracted to the Earth and the inertial mass of the body. This property of the gravitational force was discovered by Galileo, who showed that the acceleration of a falling body does not depend on its structure or its mass. On the basis of the experimental results of Galileo, later repeated much more accurately at different locations on the Earth, Einstein proposed the equivalence principle. According to this principle, there is no criterion by which inertial forces can be distinguished from gravitational ones. In other words, it is impossible to design a local experiment which can distinguish effects due to the gravitational field from effects in a coordinate (laboratory) frame moving with constant acceleration.

Now to derive the gravitational shift of a γ quantum we assume that a γ quantum is emitted from a source located at a height h above a detector, and that after some time this γ quantum is recorded by the detector. We assume that the gravitational field is uniform in the vicinity of the source–detector and that all objects in free fall undergo acceleration g. According to the equivalence principle, in the absence of a gravitational field the result of any experiment must be the same as that if the laboratory frame (in which the source and detector are located) is moving upward with acceleration g. The time needed for the γ quantum to travel the distance from the source to the detector is h/c. During this time the detector moving upward will have velocity equal to gh/c. As a result of the first-order Doppler effect, the detector measures an increase of the frequency of the γ quantum. The relative increase of the frequency will be

$$\frac{\Delta\nu}{\nu}=\frac{gh}{c^2}, \tag{1}$$

Then, according to the equivalence principle, the effect of gravitation leads to the same increase of the γ frequency. Conversely, if the source is located at height h above the detector and moves with velocity gh/c, the effect of gravitation vanishes.

Several different groups around the world independently proposed that the Mössbauer effect be used to measure the gravitational red shift under terrestrial conditions. Pound and Rebka submitted an article on this to Physical Review Letters on 15 October, 1959 (Ref. 2). Barit, Podgoretskiĭ, and Shapiro submitted one to Zh. Éksp. Teor. Fiz. on 4 November, 1959 (Ref. 3), and Schiffer and Marshall submitted one to Physical Review Letters on 23 November, 1959 (Ref. 4). It should be noted that in the article of Barit, Podgoretskiĭ, and Shapiro it was mentioned for the first time that the Möss-

bauer effect could also be used to observe the second-order relativistic Doppler effect.

The development of Mössbauer spectroscopy on the 93.3-keV γ line of the isotope ^{67}Zn is of particular interest for measuring small energy shifts. The reason is that the width of the first excited level from which the transition of energy 93.3 keV occurs is 5×10^{-11} eV. The relative width of this level is 5×10^{-16}. Compared with the width of the first excited level of energy 14.4 keV of the most popular Mössbauer isotope ^{57}Fe, the width of the 93.3-keV level in ^{67}Zn is two orders of magnitude smaller, and the relative width is about 600 times smaller.

In experiments in which the hyperfine splitting of nuclear levels is manifested, the accuracy in determining the distance between components of the hyperfine splitting depends on the width of the gamma line. However, in experiments in which the shift of a single gamma line or of the entire resonance spectrum is studied, for example, in the case of the gravitational red shift, the sensitivity of the method is related to the relative width. In the case of ^{67}Zn the height of the source above the absorber which leads to a shift of the resonance line by an amount equal to the natural line width is about 5 m. For ^{57}Fe this height is about 3 km.

Therefore, at the height of the popularity of using Mössbauer spectroscopy to measure extremely small frequency shifts, the efforts of many experimentalists focused on discovering the resonance absorption of γ quanta in ^{67}Zn. This was the case in Russia with the Dubna group at the Laboratory of Neutron Physics directed by Shapiro. In the United States there were two groups: Pound and Rebka at Harvard and the Los Alamos group. Pound and Rebka, using a series of crystal lattices, did not observe the resonance effect in ^{67}Zn with an accuracy of 0.1% (Ref. 5). This was first done successfully by the Los Alamos group.[6]

The authors of that study[6] used an original method for destroying the resonance. They rejected the usual method of Doppler modulation and used a magnetic field to obtain the resonance line. The source and absorber were made of polycrystalline zinc oxide. Zinc oxide enriched in the isotope ^{67}Zn was used for the absorber. The experiment was performed at liquid-helium temperatures. The magnetic field acted only on the absorber, since the source was enclosed in lead foil, and, as is well known, at this temperature lead foil is a superconducting magnetic screen. The resonance was destroyed as a result of the magnetic splitting of the levels only in the absorber. The dependence of the resonance absorption on the magnetic field strength was obtained by varying the magnetic field within several hundreds of oersteds. The maximum resonance effect was 0.3% and was far beyond the limits of error.

The Dubna group[7] also first used a magnetic field to destroy the ^{67}Zn resonance. The experiment was performed as follows. The surface of a sample of metallic zinc enriched to 33% ^{67}Zn was irradiated by protons of energy 6.7 MeV, and ^{67}Ga activity was induced in it via the (p,n) reaction. The sample was placed in a helium cryostat between pole tips creating a nonuniform magnetic field with maximum field strength near the source equal to 1500 Oe. The resonance absorption effect was recorded from the decrease of the intensity of 93.3-keV radiation passing through the sample when the magnetic field was switched on. The amplification was measured by the photomultipliers of the scintillation counters and was less than 10^{-5} when the field was switched on. As a result, it was found that at liquid-helium temperatures the resonance effect is $(2.58\pm0.84)\times10^{-2}$%.

After their unsuccessful attempt to see the resonance effect in ^{67}Zn, Pound and Rebka[8] quickly switched to ^{57}Fe. In spite of the fact that the relative line width in ^{57}Fe is 600 times larger than in ^{67}Zn, the resonance effect in ^{57}Fe for the 14.4-keV gamma line is many times larger. The highest sensitivity to the frequency shift can be obtained by working on the decreasing part of the resonance absorption curve, where the derivative of the transmission with respect to frequency is a maximum. The remarkable experiment of Pound and Rebka was carried out in a closed tower at the Jefferson Physics Laboratory at Harvard. The height of the source (0.4 Ci of ^{57}Co embedded in iron) above the absorber (iron enriched to 32% ^{57}Fe) was 21 m. As a result of the measurements, the authors confirmed[9] the predicted gravitational shift with 4% accuracy. It should be noted that in the course of measuring the gravitational shift of the γ frequency, Pound and Rebka experimentally discovered the thermal red shift, which is equivalent to the second-order Doppler effect.[10]

...In the hot July of 1960 the Second All-Union Conference on Nuclear Reactions at Low and Intermediate Energies was held at Moscow State University. Pound presented a talk entitled "On the weight of the photon," in which he discussed in detail the recent experiment on the observation of the gravitational red shift.[11] The same day, Shapiro presented a review of the Mössbauer effect in which he described the first studies in the USSR in the area of gamma-resonance spectroscopy.[7] In it Shapiro gave his own classical theory of the Mössbauer effect. The main idea of this theory is that thermal oscillations of the emitting atom lead to frequency modulation of the γ emission. In this case a large number of satellite lines appear in the emission spectrum together with the central unshifted line, owing to which gamma-resonance absorption without recoil occurs. The ratio of the intensity of this line to that of the full emission spectrum determines the probability for emitting γ quanta without recoil. The expression obtained for this probability,

$$f=\exp\left(-\frac{\langle x^2\rangle}{\lambda^2}\right), \tag{2}$$

where $\langle x^2\rangle$ is the mean squared deviation of a vibrating lattice atom from its equilibrium position and λ is the γ wavelength, exactly coincides with the probability for recoilless γ emission obtained in quantum mechanics.

After the experiment of Pound and Rebka, it was senseless for the Dubna group to compete with them to improve the accuracy using ^{57}Fe, in part because at the beginning of 1960 Pound had a source with activity equal to 400 mCi, while the first activity of ^{57}Co at Dubna was obtained barely in 1963 and amounted to only 3 mCi... . Shapiro decided to work on further improvement of the zinc method.

The first successful attempt to obtain the resonance spectrum in ^{67}Zn using the Doppler-modulation technique was

made by Alfimenkov *et al.*[12] The source and absorber were made of polycrystalline zinc oxide. The absorber was enriched in the isotope ^{67}Zn (33%). The Doppler modulator was a plate of quartz single crystal which, as is well known, possesses piezoelectric properties. The maximum speed of the source relative to the absorber was one and a half microns per second, which was sufficient to go beyond the resonance line. Velocity calibration of the drive at helium temperatures (the piezoelectric modulus of quartz was known only at room temperature) was accomplished using acoustical modulation of the γ emission. For this an additional sinusoidal voltage of frequency 80 kHz was applied to the quartz plate. However, the maximum resonance effect was at a level of 0.2%, i.e., too small for use of ^{67}Zn to measure extremely small energy shifts.

...In the summer of 1962 F. L. Shapiro organized the First Meeting of JINR Member Countries on the Mössbauer Effect at Dubna. This initiated a series of international conferences on the Mössbauer effect which rotated among these countries. Shapiro was interested in nontrivial experiments. He said that the experiments on the Mössbauer effect performed at Dubna should be ones which could not be performed elsewhere. The smallness of the resonance effect in ^{67}Zn certainly cooled his initial enthusiasm, and gradually he began to take less interest in the Mössbauer effect.

In 1963 I returned to Bulgaria and decided to continue the Mössbauer studies begun in Dubna. Let me describe in detail one experiment that we performed, which, in my opinion, is a nontrivial one. It is well known that atoms in a crystal undergo two types of motion: vibrational motion about their equilibrium position and diffusion jumps. If an emitting atom undergoes a diffusion jump and if the time between diffusion jumps is comparable to or less than the lifetime of the excited state, the gamma line of the emission is broadened.

Krivoglaz[13,14] studied the problem theoretically and showed that diffusion broadening depends on the angle between the wave vector of the γ quantum and the direction of the jump. Owing to the geometrical order in a single crystal, diffusion jumps occur in strictly defined directions and, depending on the diffusion mechanism, various dependences of the diffusion broadening on the angle between the γ wave vector and the crystal axes can be obtained.

The experiment was performed in the following manner.[15] A wafer was cut from a single crystal of copper in the (100) plane, and by electropolishing the thickness of the wafer was reduced to 60 microns. ^{57}Co with an activity of 25 mCi was introduced into the wafer. The diameter of the active spot was 6 mm. The sample was annealed for 24 hours at 900 °C in a hydrogen atmosphere. The source prepared in this manner was placed in an oven specially constructed for this purpose,[16] which allowed the crystal to be rotated during the experiment about the direction of propagation of the γ quanta. The absorber, at room temperature, was sodium ferrocyanide, which has a single absorption line. The Mössbauer spectra were taken for various orientations of the single-crystal wafer relative to the γ-quantum direction at a temperature of 1030 °C (only 30 °C lower than the melting temperature of copper). The sample temperature was held constant with an accuracy of 0.2 °C for 24 hours. As a result, a marked orientational dependence on the angle between the direction of the γ quantum and the (100) crystal axis was obtained. Comparing this orientational dependence with the theoretical one, it was shown directly that the vacancy mechanism of diffusion occurs in copper, and that diffusion jumps occur primarily in the first coordination sphere. Similar experiments were later performed using aluminum.[17,18]

At the beginning of the 1980s, following to some extent the legacy of Shapiro, I decided to return to ^{67}Zn and again try to measure extremely small energy shifts. The experiment was again performed at Dubna. It should be noted that although there exist isotopes in nature which have levels with widths a few orders of magnitude smaller than those in ^{67}Zn, the isotope ^{67}Zn still represents, in all probability, a limiting case in the sense of the possibility of obtaining a resonance line of natural width experimentally. As Pound noted,[19] experiments on the nuclear magnetic resonance in solids can give information about the lower limit on the line width. It turns out that it is very difficult to obtain a line width smaller than 1 kHz in such experiments.

Line broadening is a consequence of a nonuniformity in the crystal fields arising from a defect in the crystal structure or from magnetic disorder. The natural width of the 93.3-keV line in ^{67}Zn is 12 kHz. Therefore, for the line broadening not to exceed 2–3%, the source and absorber must be made of pure materials with as perfect a structure as possible.

Vetterling and Candela[20] indicated another possible mechanism for resonance line broadening related to irregularity in the distribution of the Mössbauer isotope. For example, it is known that ^{67}Zn makes up 4.1% of naturally occuring zinc. In the crystal lattice of a given zinc compound the ^{67}Zn nuclei are distributed completely randomly, so that the isotopic and, consequently, the mass neighborhood of each ^{67}Zn nucleus will be different. Interatomic forces must be independent of the mass neighborhood, but this cannot be said of local vibrations of atoms, including the zero-point vibrations. It is well known that it is these vibrations of the lattice atoms which are responsible for the thermal red shift. However, this mechanism has not been seen experimentally, and so the question of whether or not it exists must be considered open.

The technique for Mössbauer studies using ^{67}Zn was gradually improved over time. De Waard and Perlow made a multi-element quartz drive.[21] Quartz rings were arranged in the form of a stack and oriented in such a way that the amplitudes of oscillation of all the rings added. Perlow further improved the quartz drive by using the reverse transverse piezoeffect.[22] Using a drive of similar construction, Forster *et al.*[23] increased the velocity range to 200 μm/sec.

Griesinger *et al.*[24] made a piezoelectric drive using the piezoceramic PZT. Since the piezoelectric modulus of PZT ceramic ranges from 15×10^{-12} m/V to 40×10^{-12} m/V at liquid-helium temperatures, while that of quartz is 2×10^{-12} m/V, a drive made from the piezoceramic is more compact. The maximum velocity obtained using this drive was 225 μm/sec.

Feedback is not used in Doppler modulation based on the piezoelectric effect. This is because the frequency char-

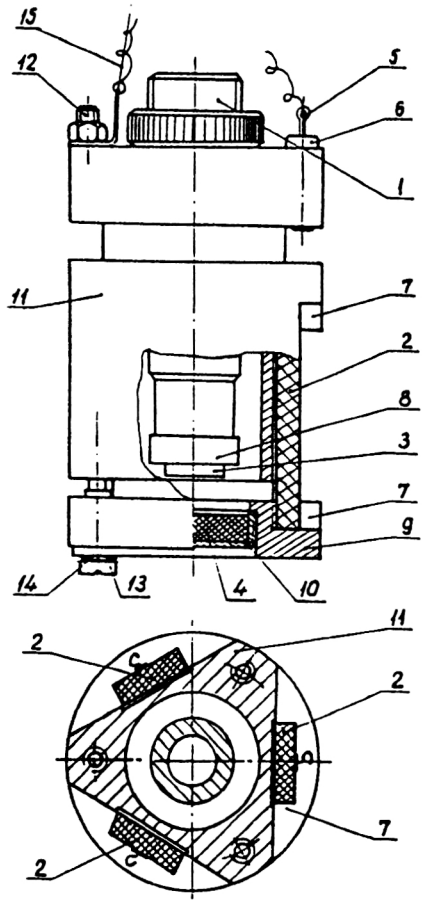

FIG. 1. Drive with a quartz piezoelectric motor: (*1*) Shaft; (*2*) quartz plates; (*3*) source; (*4*) absorber; (*5*) driving voltage; (*6*) teflon insulator; (*7*) macrolon clamps; (*8*) source holder; (*9*) moving part of the drive with recess for the container; (*10*) absorber container; (*11*) drive frame; (*12*) ground; (*13*) screws regulating the spring tension; (*14*) springs of beryllium bronze; (*15*) cotton string.

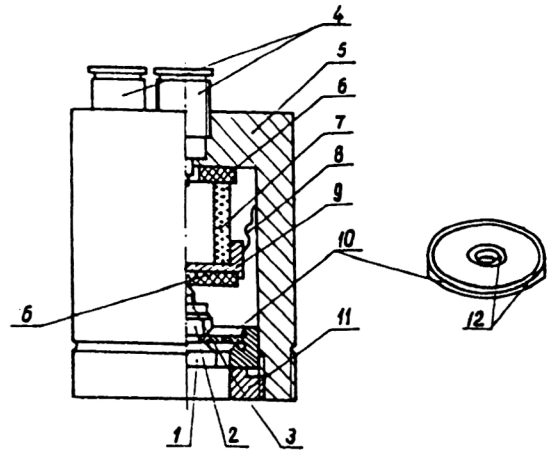

FIG. 2. Piezoceramic drive: (*1*) Source holder; (*2*) washer; (*3*) nut; (*4*) "lemo" joint; (*5*) drive frame; (*6*) parallel quartz plates; (*7*) piezoceramic cylinder; (*8*) screen made of aluminum foil; (*9*) steel container; (*10*) sensor, piezoceramic washer; (*11*) nut; (*12*) silvered electrodes.

acteristic of a motive piezoelement contains very many high-frequency resonances, which can easily be excited when there is feedback. Therefore, in the case of ^{67}Zn spectroscopy both the drive and the electronics associated with it should have very stable operation. External interference distorting the law of motion of the drive is always possible, and so continuous monitoring of the law of motion is very desirable.

Ikonen *et al.*[25] made a SQUID-based displacement sensor, which they used to check the operation of the piezoelectric drive used for spectroscopy with ^{67}Zn. The authors of that study state that the magnetic field from the permanent magnet forming part of the measurement system slightly broadens the resonance line. In addition, this method is too sensitive and too complex to use for continuous monitoring of the motion.

In Fig. 1 we show a drive in which quartz elements are used.[26,27] The construction of this drive is very close to that used by Forster *et al.*,[23] but the tubular construction of the main body of the drive proposed here is better from the viewpoint of the frequency characteristic.

A sinusoidal voltage is fed simultaneously to the YZ surface of three quartz plates. The quartz plates must be oriented in such a way that they operate in phase. The oscillations along the X axis are proportional to the applied voltage, and those along the Y axis are amplified by a factor of L_y/L_x (where L_y is the length and L_x is the thickness of the plate). In our case $L_x=3$ mm, $L_y=78$ mm, and $L_z=10$ mm. The mountings of insulating material (plastic, teflon, macrolon) serve only to center the plates. The tension in the springs (beryllium bronze or stainless steel, 1 mm thick) must ensure that the moving part of the drive follows the contraction and expansion of the quartz plates. It is best if this tension and the motion of the moving part of the drive in general are monitored by a displacement sensor.

In Fig. 2 we show a Doppler modulator based on a cylindrical piezoceramic.[26,27] All the surfaces of the cylinder (of diameter 12 mm, height 10 mm, and thickness 1 or 2 mm) were subjected to additional polishing in order to make the cylindrical surfaces as nearly coaxial as possible and the faces as parallel as possible. Radial polarization was accomplished after the polishing. In this drive the role of the springs is played by a piezoceramic washer (inner diameter 4 mm, outer diameter 15 mm, and thickness 1 mm) acting as a displacement sensor. Stress of the washer is produced by means of a micrometer screw. Deformation of the washer at its inner and outer circumferences gives rise to tangential strains which make it more highly sensitive to displacements than a sensor whose operation is based only on curvature. With this sensor the error in measuring the displacement is 4×10^{-12} m.

Potzel *et al.*[28] obtained an experimental resonance line of ^{67}Zn with width close to the natural width. Here the source and absorber were made of single crystals of zinc oxide with the naturally occurring mixture of isotopes.

Not only the material but also the technique of preparing the source is important for obtaining a narrow resonance line. Better results are obtained if a plate of single-crystal zinc oxide is irradiated by deuterons of energy 10–15 MeV. The parent isotope ^{67}Ga is usually obtained from the reaction ^{67}Zn$(d,n)^{67}$Ga. The deuteron flux is restricted by the cooling of the target. A target of zinc oxide is cooled either by gaseous helium, in which case it is best to use a closed cooling

cycle, or by running water. In both cases the chamber in which the target is located is separated from the vacuum space of the cyclotron by a thin foil (for example, of tantalum or aluminum). If running water is used for cooling, the deuteron energy must be considerably higher, so that the residual energy of the deuterons passing through the water layer will be at least 10–15 MeV.

The radiation damage to the ZnO after the irradiation must be repaired by annealing the target. Usually the annealing is done in the temperature range from 700 to 1200 °C in air or in an oxygen atmosphere.[28,29] It has been reported that quenching in water after annealing improves the quality of the source.[29] However, further studies did not confirm this result. Better sources are obtained if after irradiation a single-crystal plate of zinc oxide is annealed in an atmosphere of oxygen for 12 hours at 700°, followed by slow cooling to room temperature for 10 hours.[25,28] Zinc oxide is nonstoichiometric in the sense that the quantity of zinc exceeds the quantity of oxygen by 0 to 50 ppm. At temperatures above 1200 °C the nonstoichiometry is increased as a result of volatilization of the oxygen.[30]

Single crystals of zinc oxide, especially thin plates, are usually transparent with a slightly yellow-green tint. After irradiation the plate acquires a brownish-red color. Annealing restores the original color of the plate. Sometimes the radiation defects obtained as a result of exposure are so strong, for example, for poor cooling of the target, that the color is not restored after annealing.

An experiment using the isotope ^{67}Zn is also difficult because the energy of the gamma transition is relatively large, while the atomic mass is relatively small. This means that the probability of emitting a γ quantum without recoil will also be small. For example, if the temperature of the Debye matrix is of order 300 K, even at a temperature of 4.2 K the expected value of this probability is 1.5%. In particular, the maximum value of this probability is obtained for zinc oxide at 4.2 K and is 2%.

Consequently, when the transmission method is used, as it has been in all the experiments performed so far, the resonance depth is even smaller than this value. At the present time the experimental resonance effect lies roughly in the range from 2×10^{-4} to 10^{-2}, depending on the material of the source and the absorber. To obtain good statistical accuracy for such a small resonance effect it is necessary to record a large number of the γ quanta which have passed through the resonance absorber. If we take into account the fact that the half-life of ^{67}Ga is about 3 days, it is desirable to work with a large counting rate (2×10^5 to 3×10^5 pulses/sec or more for the 93.3-keV line without noticeable worsening of the energy resolution of the detector circuit).

Of course, the long time needed to obtain the necessary statistical accuracy can be decreased by working with many sources of smaller activity, changing them every 2 to 3 ^{67}Ga half-lives. But then at the start of each set of measurements it is necessary to obtain a reference Mössbauer spectrum in order to check the source quality. The point is that it is not always possible to completely avoid radiation damage in sources, in spite of annealing after irradiation.

The quality of the absorbers used in experiments with ^{67}Zn depends strongly on the quality of the material and also on the method of preparing it. Katila *et al.*[30] report that mechanical grinding of zinc oxide can lead to complete loss of the resonance effect.

It should not be forgotten that since the fraction of ^{67}Zn in the natural mixture of isotopes is 4.1%, it is often necessary to work with absorbers enriched with ^{67}Zn. This will certainly be the case until a source with a relatively large Debye–Waller factor is made.

In order for resonance absorption of ^{67}Zn to occur, in addition to the special requirements on the materials from which the source and absorber are made, it is necessary to reduce every kind of acoustical interference to a minimum. The level of acoustical noise must be 3 orders of magnitude lower than the level allowed in the case of a resonance absorber made of ^{57}Fe.

Returning again to the measurement of extremely small energy shifts, let me comment on an experiment to seek the electric dipole moment of the photon.

First, it should be noted that new physics can be sought in two essentially different areas. One is high-energy physics, where various types of new particles with unusual properties are created in accelerators. For example, the violation of time (T) parity (or, equivalently, combined CP parity) was first discovered experimentally in decays of K^0 mesons. Recently there has been intense discussion of the possibility of observing CP violation in B-meson decays in connection with plans for B factories.[31]

The second area is that of precision measurements of several of the fundamental characteristics of elementary particles. In this case new physics is "hidden" in hyperfine interactions, the measurement of which requires a considerable amount of experimental ingenuity.

As noted some time ago by Landau,[32] the observation of an electric dipole moment of an elementary particle is a direct demonstration of P- and T- (or CP-) parity violation. The possibility of observing the electric dipole moments of fermions (protons and neutrons) is often discussed in the literature.[33] Only recently have discussions begun about CP-violating interactions of the vector W and Z bosons (see Ref. 31 and references therein).

As far as the electric dipole moment of the photon is concerned, if it exists, it would be a new fundamental characteristic. On the one hand, the existence of an electric dipole moment of the photon implies CP violation, and on the other it leads to the assumption that a 3-photon interaction vertex exists.[1)] Such an effective interaction can be written in gauge-invariant form. However, the Standard Model of electroweak interactions would most likely have to be reconsidered. We recall that in the standard quantum electrodynamics there is a 4-photon effective interaction arising from the 4-photon box diagram. At low energies of the interacting photons it is described by a Heisenberg–Euler effective Lagrangian (see Ref. 34). Here CP symmetry is conserved. The 3-photon interaction is absent in QED (the Furry theorem), owing to conservation of charge parity. The existence of a 3-photon interaction (violating CP invariance) can be associated with the existence of internal structure of the photon.

There have been several studies in which the dipole mo-

ments of elementary particles have been sought. An upper bound of order $5\times10^{-25}e\cdot$cm has been placed on the neutron electric dipole moment.[33,35] In the case of the photon the upper bound obtained for the electric dipole moment is $10^{-10}e\cdot$cm (Refs. 36 and 37). We have devised an experiment to seek the photon electric dipole moment. The basic idea of it is as follows.[38,39]

If the photon possesses an electric dipole moment d, then in interacting with a nonuniform electric field E it would change its energy by an amount

$$\int_{z_1}^{z_2} d_z \frac{\partial E_z}{\partial z}\, dz = d(E_2 - E_1), \tag{3}$$

where z is the direction of propagation of the photon and E_1 and E_2 are the electric fields at the photon emission and absorption points, respectively.

It should be noted that the photon electric dipole moment could be an intrinsic characteristic whose value does not depend on the electric field but could be induced by such a field. Then Eq. (3) would have to be replaced by

$$\int_{z_1}^{z_2} d_z(z) \frac{\partial E_z}{\partial z}\, dz = \bar{d}(E_2 - E_1), \tag{4}$$

where $\bar{d}$ is the average value of the induced dipole moment of the photon.

Incidentally, Eqs. (3) and (4) are the classical estimates of the change of the photon energy based on the assumption that the photon behaves as a classical dipole in an external nonuniform Coulomb field E. In quantum language this change of energy can be related to the final-state interaction. The Coulomb deformation of the energy spectrum of β electrons in nuclear β decay is calculated in a similar manner (see, for example, Ref. 40).

Since the value of the photon dipole moment, if it exists, is extremely small, to find the change of the photon energy the electric fields must be very large, and the measurement methods must be extremely sensitive. Therefore, to measure the energy shift we applied the method of the gamma–nuclear resonance to the isotope ^{67}Zn. In this isotope an experimental "resolution" (ratio of the measured energy shift to the photon energy) of 3×10^{-18} is obtained.[41]

Regarding the inhomogeneous electric field, it can be obtained artificially,[36,37] but it is best to turn to Nature itself for obtaining extremely large fields. For example, the electric field near a nucleus is many orders of magnitude larger than the fields which can be created in the laboratory.

Let us consider an ordinary experiment on gamma-resonance absorption in ^{67}Zn. A photon of energy 93.3 keV is emitted by a source (a ^{67}Zn nucleus in the first excited state) and absorbed by the same nucleus in the ground state. Right after the emission the photon is in the electric field E_1 of the stable nucleus ^{67}Zn. Right before the resonance absorption the photon is in the electric field E_2 of the absorbing nucleus. If these electric fields are not the same, it follows from (3) and (4) that there must be an energy shift.

Different fields at the photon emission and absorption can be created by using the fact that the ^{67}Zn nucleus possesses a quadrupole moment Q, i.e., it is not spherical. It can

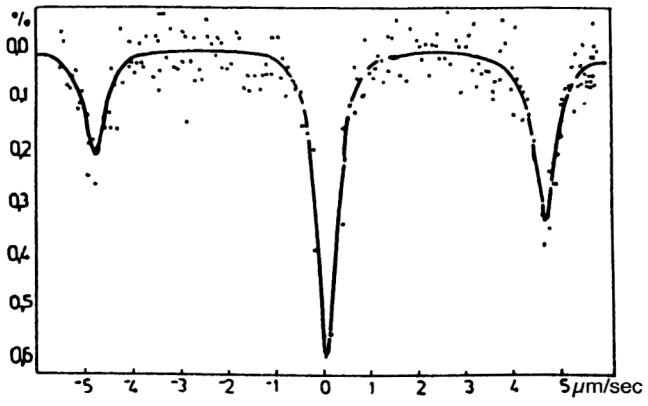

FIG. 3. Resonance spectrum of zinc oxide.

be treated as a uniformly charged ellipsoid of revolution. In this case the electric field outside the ellipsoidal nucleus in the direction of the major axis will differ from the electric field in the direction of the minor axis. Now if we assume that in the source the ^{67}Zn nuclei are aligned in the direction of propagation of the γ quantum, and in the absorber the ^{67}Zn nuclei are aligned perpendicular to this direction (or vice versa), a shift of the resonance line must be observed.

Resonance spectra for the isotope ^{67}Zn have been obtained by the transmission method. In Fig. 3 we show the characteristic resonance spectrum when the source and absorber are made of zinc oxide.

The source was obtained by irradiating a single-crystal plate of zinc oxide (diameter 8 mm, thickness 1 mm, axis c perpendicular to the plane of the plate) with deuterons of energy 12.6 or 15.6 MeV. During the exposure the plate was cooled by gaseous helium. After the exposure the source was annealed at a temperature of 700 °C in an oxygen atmosphere for 12 hours and was then slowly cooled.

The resonance spectrum in Fig. 3 was obtained with an absorber of polycrystalline zinc oxide, enriched to 92% in the isotope ^{67}Zn, with a thickness of 0.785 g/cm^2 in ^{67}Zn. The line width near zero velocity of the source was 0.49 ± 0.04 μm/sec. We used this spectrum to calibrate the energy scale; the known quadrupole splitting in zinc oxide was used.[42] All the measurements were carried out at liquid-helium temperatures. To decrease the effect of external acoustical vibrations the Doppler modulator was suspended on three cotton strings, and the heat exchange was effected by gaseous helium at a pressure of 10^3 Pa. The entire cryostat together with the heavy platform was acoustically isolated from the support, which was attached to the laboratory wall.

To search for the photon dipole moment, two spectra were measured. The absorber was made of single-crystal zinc oxide with the natural mixture of isotopes. In one case the resonance spectrum was recorded when the axes c,c' in the source S and absorber A were parallel, with the two axes in the same direction as the γ momentum. In the second case the resonance spectrum was measured when the axis c' in the absorber was rotated by 90°. Here the γ momentum remained parallel to the axis c in the source. The spectra

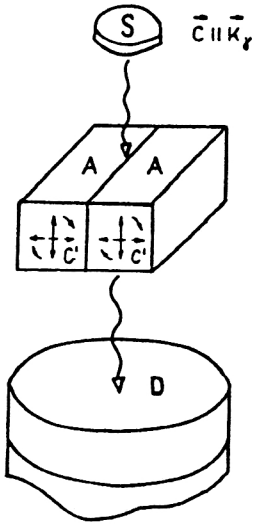

FIG. 4. Design of an experiment with two crystals.

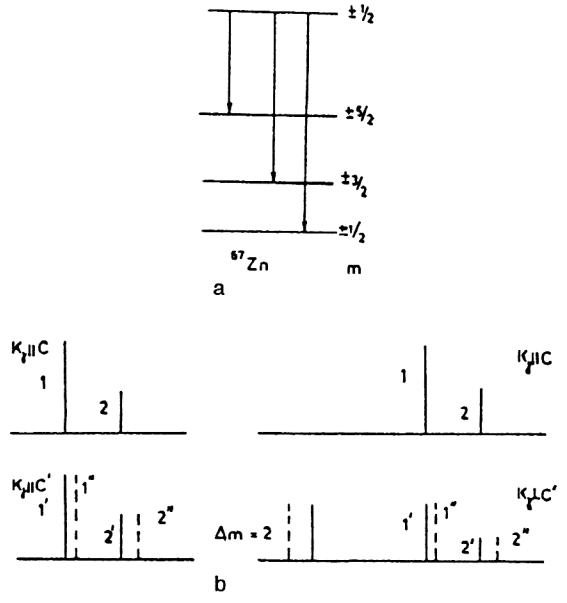

FIG. 5. (a) Quadrupole splitting of the ground state of ^{67}Zn. (b) Emission and absorption spectra of single-crystal zinc oxide.

were measured in the velocity range for which the error in measuring the resonance line shift would be a minimum. The parameters of the experimental line were determined under the assumption that the line has a Lorentzian shape.

When the axis c' in the absorber was rotated by 90°, the geometry of the experiment and the thickness of the absorber were not changed. For this the absorber was made of two identical parts which could be rotated by 90°, as shown in Fig. 4. The dimensions of the compound single-crystal absorber were $10\times10\times5$ mm. Three measurement runs were made. Each run lasted about 10 days, because the half-life of the parent isotope ^{67}Ga is 78 hours. At least three resonance spectra were taken in each measurement run: first the reference spectrum, and then two spectra with the single-crystal absorber corresponding to the two orientations of the axis c' in the absorber.

The parameters of the resonance absorption spectra with the single-crystal absorber in the three runs are given in Table I. We see from these results that when the axis c' in the absorber is rotated by 90° the resonance line always undergoes a positive shift which, although small, still falls outside a single standard deviation. Let us try to explain this shift by assuming that the photon has an electric dipole moment.

In an axially symmetric field in single-crystal zinc oxide, the ground state is split into three sublevels as a result of the quadrupole interaction (Fig. 5a). Each sublevel corresponds to a definite orientation of the ellipsoidal nucleus, which precesses about the quantization axis c (c'). As a result of the angular dependence of the relative intensities of the hyperfine-splitting lines, the emission spectrum consists of two lines, since the γ quantum is emitted in the direction of the axis c. The absorption spectrum consists of two or three lines, depending on whether the axis c' in the absorber is parallel to the γ momentum or whether it is rotated by 90°. However, the line of resonance absorption near zero velocity is obtained only for overlapping of the $1\rightarrow1'$ and $2\rightarrow2'$ lines (Fig. 5b). Therefore, right after the emission and right before the resonance absorption the ^{67}Zn nuclei in the source and absorber are arranged identically in pairs if the axes c and c' are parallel. When the axis c' is rotated by 90°, their mutual orientation is changed, and it would seem that the electric fields at the photon emission and absorption are different.

TABLE I.

No.	Orientation	Statistics N_∞, pulse/channel	Position, μm/s	Shift $\Delta=p_\perp-p_\parallel$, μm/s
1	$k_\gamma \parallel c \perp c'$	38.8×10^6	0.0158±0.0081	0.0107±0.0095
1	$k_\gamma \parallel c \parallel c'$	31.4×10^6	0.0051±0.0049	
2	$k_\gamma \parallel c \perp c'$	101.7×10^6	0.0218±0.0076	0.0094±0.0085
2	$k_\gamma \parallel c \parallel c'$	46.5×10^6	0.0124±0.0038	
3	$k_\gamma \parallel c \perp c'$	69.0×10^6	0.0094±0.0051	0.0092±0.0070
3	$k_\gamma \parallel c \parallel c'$	50.0×10^6	0.0002±0.0047	

Let us now estimate the possible value of the photon electric dipole moment. For this we first calculate the electric field outside an ellipsoidal nucleus along the major and minor axes. The quadrupole moment of the ^{67}Zn nucleus in the ground state is $Q=0.17b$ (Ref. 43). This is also the expectation value of the Q_{zz} component of the quadrupole-moment tensor for the $\pm5/2$ state. The corresponding expectation values for the $\pm3/2$ and $\pm1/2$ states are $\langle Q_{zz}\rangle_{\pm3/2}=-\frac{1}{5}Q$ and $\langle Q_{zz}\rangle_{\pm1/2}=-\frac{4}{5}Q$. On the other hand,

$$\langle Q_{zz}\rangle=\frac{2}{5}Z(b^2-a^2),\quad Z=30, \tag{5}$$

where a and b are the semiaxes of the effective charged ellipsoid (b is parallel to the axis c of the ZnO single crystal). Using the well known expression for the nuclear radius,

$$a=1.4(A)^{1/3}10^{-13}\ \text{cm},$$

for a and b we obtain

$a=5.686\times10^{-13}$ cm,

$b_{3/2}=5.661\times10^{-13}$ cm,

$b_{1/2}=5.586\times10^{-13}$ cm.

The electric-field potential outside a uniformly charged ellipsoid of revolution has the form[44]

$$\Phi=\pi\rho a^2 b\int_{\xi}^{\infty}\left\{1-\frac{x^2+y^2}{a^2+s}-\frac{z^2}{b^2+s}\right\}\frac{ds}{R_s}, \tag{6}$$

where ρ is the nuclear charge density,

$R_s=(a^2+s)(b^2+s)^{1/2}$,

and ξ is the positive root of the equation

$$\frac{x^2+y^2}{a^2+\xi}+\frac{z^2}{b^2+\xi}=1. \tag{7}$$

Differentiating (6) with respect to z and x, and taking into account the dependence of ξ on z and x, for the electric fields along the axes b and a of the ellipsoid we obtain

$$E_z=\frac{3}{2}Ze\int_{\xi}^{\infty}\frac{z}{b^2+s}\frac{ds}{R_s}=\frac{45e}{l^2}\left[2+\frac{2z}{l}\arctan\frac{z}{l}-\pi\frac{z}{l}\right] \tag{8}$$

and

$$E_x=\frac{3}{2}Ze\int_{\xi}^{\infty}\frac{x}{a^2+s}\frac{ds}{R_s}=\frac{45e}{l^2}\left[-\left(1-\frac{l^2}{x^2}\right)^{1/2}+\frac{x}{l}\arctan\left(\frac{x^2}{l^2}-1\right)^{-1/2}\right], \tag{9}$$

respectively, where $l=(a^2-b^2)^{1/2}$.

Averaging over a region near the nucleus of size of the order of the γ wavelength, and taking into account the relative intensities in the transitions $1\rightarrow1'$ and $2\rightarrow2'$, for the differences of the electric fields we obtain

$$\Delta E_{3/2}=E_{z,3/2}-E_{x,3/2}=1.5131\times10^{13}\ \text{V/cm},$$

$$\Delta E_{1/2}=E_{z,1/2}-E_{x,1/2}=6.1436\times10^{13}\ \text{V/cm}, \tag{10}$$

Then, according to (3) and (4), for the photon electric dipole moment we find

$$d\approx\frac{|\bar{\Delta}|}{\frac{5}{6}\Delta E_{3/2}+\frac{1}{6}\Delta E_{1/2}}\approx1.3\times10^{-25}e\ \text{cm}. \tag{11}$$

Here it should be noted that in the case of an intrinsic electric dipole moment of the photon it is assumed that its direction must be related to that of some other physical quantity characterizing the photon,[45] i.e., its momentum vector. Even if the electric fields E_1 and E_2 have the same absolute value, the projections of these fields on the momentum direction would be different. Therefore, the shift of the resonance line should be observed also for spherical nuclei, its sign would depend on whether the photon electric dipole moment vector is parallel or antiparallel to the wave vector k_γ, and the magnitude of the shift would depend not on the difference but on the sum of the electric fields.

As seen from Table I, in all the runs the shift of the resonance line is changed when the axis c' in the absorber is rotated by 90°, and the value of this change is roughly stable from run to run, unlike the positions $P_\parallel$ and $P_\perp$. The latter implies that the position of the resonance line is affected by another mechanism which does not depend on the relative orientation of the source and absorber.

In all probability this mechanism is related to the difference of the quadrupole interactions in the source and absorber. In fact, although we work with single crystals of zinc oxide, these crystals are not perfect. Since the resonance line in ^{67}Zn is very narrow, even a tiny deviation of the parameters of the crystal lattice can affect the value of the quadrupole splitting.[46] The absorber was not changed during the measurements, but the sources were made of different single crystals. In addition, effects arise in the irradiation which are later eliminated by annealing, but there is still some probability that the parameters of the crystal lattice can change.

If we assume that the quadrupole interaction in the source is smaller than in the absorber, the resonance line near zero velocity obtained as a result of the overlap of the $1\rightarrow1''$ and $2\rightarrow2''$ lines (Fig. 5b) will be shifted to the right (a positive shift). However, the magnitude of the shift is the same for the two orientations and does not enter into the difference of the shifts. If the quadrupole interaction in the source is larger than that in the absorber, $P_\parallel$ and $P_\perp$ must have negative sign, which does not correspond to the experimental results.

Thus, the change of the resonance line shift when the axis c' in the absorber is rotated by 90° cannot be attributed to a difference of the quadrupole interactions in the source and the absorber. Nevertheless, the error in the shift in rotating the crystal by 90° is significant, so that the estimate obtained for the photon electric dipole moment should be viewed as an upper bound.

...Shapiro was correct when in his time he persisted in improving the Mössbauer technique for ^{67}Zn. Twenty years after the experiment on the gravitational shift of the γ frequency, Katila and Riski[47] performed a similar experiment using ^{67}Zn, with the height of the source above the absorber equal to only 1 m. The accuracy of this experiment is no better than that of the experiments of Pound and Rebka and of Pound and Snider,[48] but a step was taken in the right direction.

To seek confirmation of the theory with an accuracy of 0.1% it is necessary to increase the height of the source (^{67}Zn) to several meters while preserving the intensity of the beam of γ quanta which have passed through the resonance absorber. This can be done by using a capillary gamma-optical device allowing divergent radiation to be collected into a quasiparallel beam and focused.

...I would like to conclude by saying a few words about Fedor L'vovich Shapiro. Shapiro was a man who always sought the gems in science. He grasped a new idea quickly. He did not worry about details, but this does not mean that the details, sometimes very important for the work, escaped him. I remember a lecture given at Dubna by Palevsky which Shapiro translated from English. The translation was so careful and detailed that one even had the feeling that Shapiro

had added something himself. He was very tolerant and well-disposed to us young people. One could go to him with any question at any time, during work, on the train, and so on. If he couldn't answer a question immediately, he thought about it and gave the answer in an hour or two or in a day or two. During night measurements, of which there were certainly enough, one could take a nap on the sofa in his room and, in general, when he was in Moscow he let us use his room as a quiet place to work.

If I had to characterize him briefly, I would say that he was a pragmatic enthusiast. His enthusiasm always had a forward thrust, and his pragmatism was manifested in the fact that he did everything possible under the conditions which society imposed upon him.

[1)]In general, it is also possible to write down a 4-photon effective interaction which violates CP invariance.

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