From radar to nuclear magnetic resonance

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As war engulfed Europe from September 1939, and the Axis powers overran most of the western European countries in 1940, the United States undertook to build up quickly its military capabilities. By late 1940, a full year before the U.S. was drawn into war as a combatant, there began a massive move of scientists, especially physicists, temporarily into new organizations set up to develop technologically advanced weapons. One of the first of these, destined to become one of the largest, was the ''Radiation Laboratory,'' so named with an intent to obscure its purpose, at the Massachusetts Institute of Technology, established in November of 1940 by the National Defense Research Committee (NDRC). Its mission was to develop radio detection and ranging (to become known as Radar), inspired by the startling performance of the pulsed cavity magnetron revealed to U.S. military officers and members of the National Defense Research Committee by the British ''Tizard Mission.'' Although magnetrons as generators of electromagnetic energy of short wavelength had been developed in several places many years earlier, the new magnetron was a breakthrough in that it could produce microwave pulses many orders of magnitude more intense than could anything else then in existence. It was an ideal device for the development of radar. The visit from the beleaguered British scientists and high military officers, headed by Sir Henry Tizard, had entered into this exchange of secret new military technology to try to obtain technical help and manufacturing support from US industry, relatively insulated from air attack. The cavity magnetron has been described, in view of its developed use in the war, as possibly the most important cargo ever to cross the Atlantic, although many other secret developments were included in the exchange. For example, the British progress toward releasing nuclear energy was also revealed.

Physicists, and other scientists, were recruited in very great numbers into the new Radiation Laboratory and other emergency organizations, resulting in a nearly complete shutdown of basic research. The scale is apparent from the evidence that the Physical Review published a single issue of only 54 pages for the whole month of January, 1946, its publishing nadir. That issue contained only two regular articles, both of which were reports of researches completed before the shutdown, but which saw print only after the war had ended. A large part of that issue was the ''Letters'' section that reported some early postwar activity, including our first report (Purcell, Torrey, and Pound, 1946) of the successful detection of nuclear magnetic resonance through its absorption of radio-frequency energy. An early step in the postwar rebirth of research in basic physics was thereby announced. For scale it is worth noting that in the corresponding month of January 1996, the Physical Review published nearly 8000 pages in its several parts.

Although the Radiation Laboratory was eminently successful in its technical goals and is widely recognized as having contributed importantly to the Allied victory, there were several less generally recognized effects on the postwar world of physics. Many physicists not previously greatly concerned with electronic instrumentation developed a much deeper understanding especially of the fundamental limits to instrumental sensitivity set by various sources of interfering ''noise.'' Beyond atmospheric noise, often called ''static,'' wider recognition of shot effect noise, from the electronic granularity of electrical currents, and thermal noise, explained by the equipartition theorem of statistical mechanics, were more widely understood. It was demonstrated quite early that the most sensitive device for the initial signal detection in a microwave (wavelength 10 cm and less) receiver was a developed version of the archaic ''crystal diode'' detector. This consisted of a semiconductor and a metal ''cat's whisker'' and had been superceded by thermionic vacuum tubes for serious radio uses more than twenty years before. As a result, an extensive program of research and development of semiconductors, principally silicon and germanium, was underwritten by the NDRC. The succeeding development of solid-state electronics in the postwar era is deeply rooted in the importance attached to finding and making reliable the best detectors for microwave radar in the war years.

Perhaps as important as any direct technical progress was a long-lasting effect of the personal interactions produced by this temporary relocation to one large organization of a large fraction of the active research physicists who had already achieved important results in widely diverse areas at many institutions. In the two decades between the world wars there had been much progress in such fields as nuclear physics, where accelerators, including Van de Graaf's belt electrostatic generator and cyclotrons, as devised by E. O. Lawrence, were coming into use in several institutions. The study of cosmic rays was the focus of several groups and, of course, the discovery of neutron-induced fission of ^{235}U, just as W.W. II was beginning, is well known. The elegant rf resonance techniques in atomic and molecular beams developed at Columbia University in the group headed by I. I. Rabi for the study of nuclear spins and moments (Rabi *et al.*, 1938; Kellog *et al.*, 1939) had not spread significantly to groups at other institutions. An analogous technique had been developed by Felix Bloch and Luis Alvarez in California to determine the magnetic moment of the neutron (Alvarez and Bloch, 1940). Rabi

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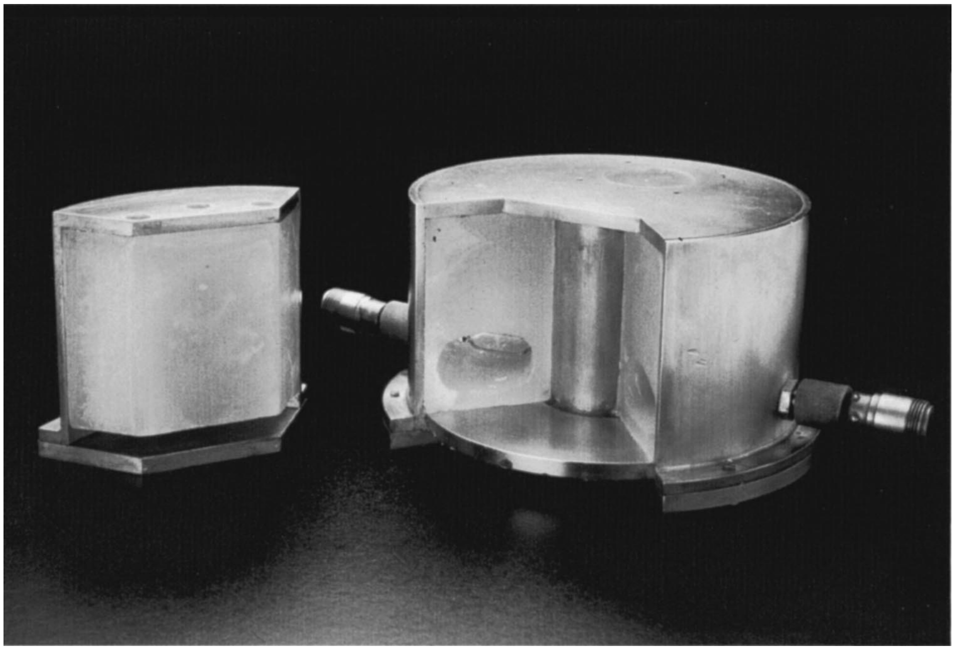

FIG. 1. The 30-MHz resonant cavity filled with paraffin as a proton sample. It is held at the Smithsonian Museum and has been cut open to reveal its inner structure.

was an early participant in the Radiation Laboratory and became an influential Associate Director and head of the Research Division for most of the five years of life of the Laboratory. Many of the members of his former group at Columbia also joined the MIT Laboratory and others at both Columbia and the Bell Laboratories were in close communication as they pursued projects in aid of those at MIT. A consequence was a much wider recognition of the achievements of the Columbia group among the main body of physicists, especially highlighted by the award of the Nobel Prize for Physics for 1944 to I. I. Rabi at a special ceremony in New York.

When the war finally ended on August 14, 1945, there began an exodus of scientists to return to their old institutions or to take up new civilian positions. However, many of the active members were asked to remain to contribute to technical books describing the advances made in secret during those five years. There was created the Office of Publications, headed by physicist Louis Ridenour, which kept many of us at MIT until June 30, 1946, to contribute to the resulting Radiation Laboratory Series of 28 volumes. Understandably our concentration on the writing projects was often diluted with thoughts about new possibilities for research that would grow from our special experiences. Henry C. Torrey, one early veteran of the Rabi team at Columbia, shared an office with me during this period. One day in September we invited Edward M. Purcell, who had headed the Fundamental Developments Group, a part of the Division headed by Rabi, to join us for lunch. As we walked from MIT to Central Square, Ed asked Henry what he would think about the possibility of detecting resonant absorption of radio-frequency energy by nuclei in condensed materials by their magnetic dipole moments, if their states of spin orientation were split by a strong applied magnetic field. Purcell has indicated that his thoughts were led in this direction by his close association with Rabi and other alumni of the Columbia group. In addition, he was writing up the discovery and the explanation of the absorption of 1.25-cm microwaves by atmospheric water vapor, a discovery that had decreased the enthusiasm for intensive development of radar systems operating on that wavelength by his group. The H_2O molecule was found to possess two energy levels, among a very large number, with an energy difference just matching the quantum energy, $h\nu$, of 1.25-cm microwaves.

Torrey's initial response at our luncheon was actually pessimistic but, after giving the question some more quantitative attention at home that evening, he convinced himself that it should be possible. When he so informed Ed the next morning, Purcell immediately proposed that we three undertake experimentally to detect such an absorption. Thus we began a spare-time project that helped lighten the dullness of the writing assignments which remained as our committed full-time employment.

Our five-year immersion in microwave technology led us to design and construct a cavity resonator to contain the test sample in a strong magnetic field. We could plan on a field only large enough to bring the resonant frequency of protons to 30 MHz, or ten meters' wavelength, hardly to be described as a microwave. I include as Fig. 1 a photograph of the coaxial cavity, cut open to reveal its innards, and now held by the Smithsonian Museum. As an open-ended coaxial resonator it would be a quarter wavelength long, 2.5 meters, but a disk insulated from the lid by a thin sheet of mica as a loading capacitance shortened it to about 10 cm. The space below the disk that should contain circumferential rf magnetic flux at the cavity resonance was filled with about two pounds of paraffin wax, chosen because of its high concentration of hydrogen and its negligible dielectric loss. Purcell's search for a suitable magnet at MIT was unrewarded, but Ed was offered by our colleague J. Curry Street the use of a magnet at Harvard he had built in the mid 1930s for bending the tracks of cosmic-ray particles in his cloud chamber. It was with this magnet that Street had measured the mass of the cosmic-ray muon (Street and Stevenson, 1937). He had joined the Radiation Laboratory at its beginning, and the magnet had been collecting cobwebs for five years. Thus our project was moved to Harvard and was carried out mostly in evenings and on weekends. The basic concept was a balanced bridge, with the cavity resonator in one arm, excited with a 30-MHz signal generator. Its transmitted signal was nearly balanced out by adjustment of the phase and amplitude sent to a common junction through a parallel arm. In this way we were able to look for very small changes in the signal transmitted through the cavity when the magnetic field was adjusted through the magnitude that should result in magnetic resonance of the protons in the cavity arm. The net signal from the bridge was amplified in a low-noise 30-MHz preamplifier, borrowed from the Radiation Laboratory, where it had been developed for the intermediate frequency amplifiers of radar receivers. The amplified signal fed into a 30-MHz communication receiver, also borrowed from my laboratory at MIT, for further amplification and was then detected and observed on a micro-ammeter as an output meter. The magnetic-field strength required for resonance was calculated from the measurements of the Rabi group of the proton magnetic moment, as about 7 kilogauss. We had added new pole caps to Street's magnet and used a flip coil and ballistic galvanometer to calibrate the field vs current, as adjusted by a rheostat in our laboratory that controlled the field current of the remote *dc* generator.

Attempts to see the absorption as a deflection on the micro-ammeter failed during a frustrating lengthy Thursday night effort and again for most of the following Saturday afternoon. However, a final run, intended to be a preliminary part of a discouraged shutdown for further thought, was made taking the magnet to the highest current available from the generator. This amounted to some 40% more than had been called for in our calibration. As we lowered the current slowly, suddenly, at about 15% above our calibration value, there occurred just such a meter deflection as we had anticipated seeing at the proton resonant field. The "signal" was clearly caused by the dip in cavity transmission we sought. We almost failed to achieve our goal because we had assumed our calibration was not in error by more than 10%. In fact, it proved to be in error by only 2%, but we had failed to appreciate that our calibration data showed that our scan over plus and minus 10% in current covered less than a 2% excursion in field strength. That resulted from the iron core of the magnet severely saturating at these currents. So, happily, the project succeeded on Saturday afternoon, December 15, 1945, as a pencilled note in the hand of Henry Torrey in my small, now rather tattered, notebook testifies (Fig. 2).

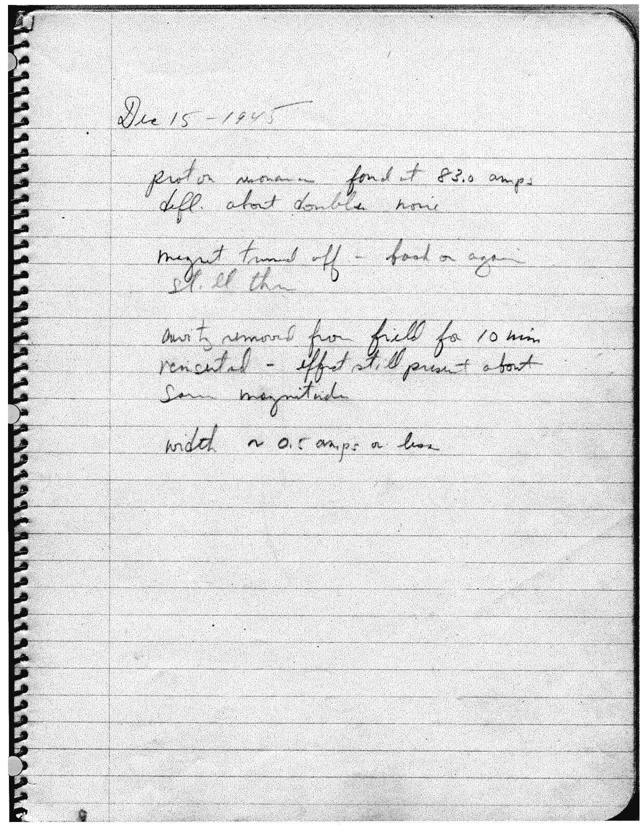

FIG. 2. The note, in the hand of H. C. Torrey, that records our successful detection of proton NMR absorption. It appears on a yellowing page of the small spiral bound notebook that served to record a miscellany of notes during the years 1942 to 1948.

In the course of our preparation for the trial we had become concerned about whether the two-level proton spin system would come to thermal equilibrium in a reasonable time, as required to obtain the magnetic polarization, or reach an energy state population difference, needed to have absorption. Without such a difference, induced emission and absorption would exactly balance and no signal would be produced. Torrey had estimated a relaxation time of some hours by adapting to apply to nuclei a theory of I Waller (1932) developed for electronic spins in crystalline materials. We had estimated that our large sample and weak rf field would allow some hours of observation of the resonant absorption without seriously overriding the thermal population differential, once that equilibrium had been established. We feared that our initial failures might be a sign that the relaxation time was too long, but were greatly relieved when we found that those failures were so easily explained. Some quick experiments showed that the thermal relaxation time of the protons in paraffin wax was shorter than the shortest time, perhaps fifteen seconds, required to bring the magnet current up from zero. This was explained in the course of the ensuing researches in this new field, as conducted at Harvard, when Nicolaas Bloembergen, a graduate student newly arrived from the Netherlands, joined Purcell and me in the enterprise. We carried out the work that formed Bloembergen's thesis at Leiden, which became widely known as BPP (Bloembergen, Purcell, and Pound, 1948), and which explains the spin-lattice relaxation and averaging out of line-broadening interactions by internal motions and fluctuations especially dominant in liquids. Paraffin wax clearly possesses considerable internal molecular motions and has a spin-lattice relaxation time on the order of milliseconds.

In the course of our initial experiment we learned that C. J. Gorter in Holland had reported failed efforts to detect NMR, first calorimetrically in 1936 (Gorter, 1936), and then by electronic frequency pulling resulting from the dispersion that should accompany absorption (Gorter and Broer, 1942). Had we been aware of these reports at the beginning we might have been discouraged from undertaking the project, but access to the wartime Dutch publications in 1945 was limited because of the only recently ended German occupation. We also heard, near the culmination of our project, that Felix Bloch and W. W. Hansen were making a similar effort at Stanford University. Hansen had served as a consultant on microwaves to the MIT Radiation Laboratory from its beginning, giving weekly lectures, traveling up from his wartime base at the Sperry Gyroscope Company on Long Island, New York. Bloch spent a couple of years at the radar countermeasures laboratory at Harvard. Both had, however, returned to Stanford and had begun their nuclear resonance project early in 1945. They reported observing the resonance of protons by a technique they named "nuclear induction" in a short letter (Bloch, Hansen, and Packard, 1946) submitted to the editor about six weeks after ours. Their approach sensed the precession of the macroscopic nuclear polarization rather than absorption. The relationship between these different ways of observing the same basic resonance was only properly understood sometime later. Not all two-level systems that can be observed in absorption actually involve macroscopic precession, however. For example, absorption at energy state differences created by nuclear electric quadrupole interactions with crystalline electric fields does not involve precession. Studies of "nuclear electric quadrupole resonance" in solids have much in common with NMR for nuclei of spin greater than 1/2, which includes a majority of the nuclear isotopes.

In the beginning the main motivation for pursuing NMR had been as a way to study spins and moments of nuclear isotopes. Although that aspect occupied the attention of many researchers, properties of the resonance provide evidence of the effects of the environment of the nuclear spins in materials. Because of the motional narrowing, as explained by BPP, results in resonance lines for hydrogen often fractions of a Hertz in width, very small chemical shifts, and complex resonance line structures have turned out to provide a tremendous source of new information on molecular and crystalline structure. NMR has become a powerful tool in chemical analysis, materials science, and, recently, as the basis of MRI (magnetic resonance imaging) in medicine. Through linewidth studies, relaxation-time observations, and small frequency shifts of chemical and condensed-matter origin, NMR has come to provide a window into the workings of many materials, including the human body.

An extension of ideas originating in NMR led to a realization that the effects that give rise to line structures and to spin-lattice equilibrium play a role in a seemingly unconnected field, the study of the correlation in direction of the emission of successive radiations from excited nuclei (Abragam and Pound, 1950). In addition to magnetic interactions, NMR allowed observation of the effects of electric fields on nuclei through the nuclear electric quadrupole moments of nuclei of spin one or more (Pound, 1950). Thus, if intermediate states in nuclear decay are not extremely short lived, those interactions cause reorientations before a succeeding decay, resulting in a departure from the expected directional correlation. Study of these disturbances, especially as a function of time after the initial decay, has yielded a way to determine properties of the nuclear moments and of the environment of short-lived isotopes. That work goes under the acronym TDPAC for time-delayed perturbed angular correlations.

Another phenomenon relating to NMR came from the discovery of recoil-free resonance of gamma rays by nuclei bound in crystals, as reported by Rudolf Mössbauer (1958a, 1958b) for ^{191}Ir in iridium metal. In 1959 the technique was extended to a 14-keV gamma ray from an isotope of iron, ^{57}Fe, that follows the decay of 270-day ^{57}Co to iron (Pound and Rebka, 1959; Schiffer and Marshall, 1959) in a stable ground state. In this case the resonance phenomenon was truly "nuclear," in that gamma rays were emitted and absorbed by nuclei. The binding of the nuclei to crystalline sites in a lattice turned out to reduce to negligible importance the broadening from the Doppler effect from thermal vibration, because the component of the atomic velocity along the direction of emission or absorption, averaged over the life of the excited nuclear state involved, vanishes for the atom bound to a lattice site. In this scheme gamma rays emitted from a crystalline source are sent through a crystalline absorber containing bound nuclei in the ground state to which the radiation leads. The transmission is observed as a function of applied relative motion, which Doppler shifts the gamma-ray frequency. These resonances turn out to be fractionally so narrow that hyperfine structures are resolved and evaluated. Even the minute effect of gravity on the relative frequency of gamma rays of nuclei held at elevations differing by only a few meters, an energy shift of only a part in 10^{15}, has been demonstrated with a precision of one percent (Pound and Rebka, 1960; Pound and Snyder, 1965). With the introduction especially of ^{57}Fe, gamma-ray resonance spread into many areas of physics, chemistry, and even biology, providing yet another window on the detailed inner secrets of materials.

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