Achievements and Current, Problems of Solid-State Radiospectroscopy (From the Materials of the 17th Ampere Congress, Turku, Finland, August 21-26, 1972)

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A substantial expansion of the possibilities of solid-state radiospectroscopy has occurred in recent years. It is mainly based on the results of fundamental studies on the dynamics of paramagnetic spin systems. Since, as we know, the magnetic-resonance methods (electron (EPR), nuclear (NMR), acoustic (APR), electron-nuclear double resonance (ENDOR), nuclear quadrupole (NQR), etc.) are widely applied in science and technology, it seems useful to acquaint the readers of this journal, however briefly, with the fundamental achievements of recent years and with some current problems in this field.

While mainly following the materials of the recent 17th AMPERE Congress, which is the most prestigious conference on radiospectroscopy, we shall adduce also some additional material needed for clarity of presentation. On the other hand, in line with the fundamental aim of these remarks, we shall concentrate attention only on the newest and most interesting problems, while abstaining from detailed illumination of traditional lines of research. As a rule, the bibliography includes only the newest studies, which are as much as possible of a review nature.

A characteristic feature of modern solid-state radiospectroscopy is the ever wider use of dynamic methods based on representing the quantization of spin systems in a rotating frame of coordinates (RFC), combined with the modern concept of the spin temperature.[1-3] We can consider the most important consequences of applying these ideas to be the sharp elevation in the sensitivity and resolving power of solid-state NMR spectroscopy.

The possibility of detecting NMR (and NQR) signals from spins (S) that are present in very low amount (or which have a small magnetic moment) is based on energy exchange between them and the nuclear spins of another type (I) whose concentration in the same material suffices for reliable observation of resonance. Since the Larmor frequencies ω_S and ω_I of the spins S and I in the external magnetic field H_0 differ, there is no contact between them under ordinary conditions, and one uses resonance in a RFC to establish it. As we know (see, e.g.[1]), the behavior of a spin system situated in the field H_0 (lying along the z axis) and a sufficiently strong high-frequency field $2H_1 \cos \omega t$ perpendicular to it ($\omega \approx \omega_0 = \gamma H_0$, where γ is the gyromagnetic ratio of the paramagnetic particle) is adequately described in a frame rotating about z at the frequency ω. Here the "effective field" $H_{eff} = \{[H_0 - (\omega/\gamma)]^2 + H_1^2\}^{1/2}$ plays the role of the constant magnetic field, and it forms the angle $\theta = \tan^{-1}\{H_1/[H_0 - (\omega/\gamma)]\}$ with the z axis. In order to make the spins S and I interact, two high-frequency fields are applied to the specimen whose amplitudes and frequencies cause the resonance condition to be satisfied in the "effective fields":[4] $\gamma_I (H_{eff})_I = \gamma_S (H_{eff})_S$.

Let us impart beforehand by one of the known methods[3] to the system I a low spin temperature in the RFC. Then this interaction will cause a considerable "cooling" (i.e., polarization) of the spins S, which will thus facilitate their detection.[5] On the other hand, application of non-adiabatic variations of the saturating field at the frequency ω_S will "heat" the I spins, and this can also be detected by standard methods.[4] The development and perfection of this methodology (in particular, one can go from the original pulsed variant to a continuous variant, and replace exact resonance in the "effective fields" with thermal contact of the S spins with a refrigerated system of dipole spin-spin interactions having a quasicontinuous spectrum[6,7]) permits one currently to detect resonance signals of nuclei whose relative concentration is less than $10^{-3}\%$. This is about three orders of magnitude better than the sensitivity of ordinary NMR. This makes it possible to gain unique information on electric-field gradients near impurities and structure defects,[7] to determine the magnetic moments of rare isotopes (e.g., ^{40}K[6]), etc.

Another major achievement of modern NMR spectroscopy is the development of high-resolution NMR methods in solids. As we know, the width of NMR lines in solids is relatively large ($\sim 10^4$ Hz), and it is determined by magnetic dipole-dipole interactions among the spins. In order to diminish this broadening, one uses the fact that the most important ("secular") part of the dipole-dipole interaction between the spins i and j is proportional to the quantity $(1 - 3\cos^2\theta_{ij})$, where θ_{ij} is the angle between H_0 and the line between the interacting spins. When $\theta_{ij} = \cos^{-1}(1/\sqrt{3}) = \theta_M$ (θ_M is the "magic angle"), this quantity vanishes, and a sufficiently rapid rotation of the specimen about an axis is inclined at the angle θ_M to H_0 will average out the dipole-dipole interaction and thus sharply diminish the line width. This method has now been brought to a level that permits improving the resolution to amounts of the order of 2×10^{-6} and determining with high accuracy the Knight shifts of different isotopes and the parameters of indirect nucleus-nucleus interaction in metals.[8]

However, another approach is even more effective, which replaces mechanical rotation of the specimen by rotation of its magnetic moment about the field H_{eff} in the RFC at $\theta = \theta_M$ (see, e.g.[9]). In this case suppression of dipole broadening is not accompanied by spatial averaging of the anisotropic chemical-shift tensor. This permits one to use NMR spectra to determine the nature and direction of chemical bonds in solids. In the current variants of this method, the material under study is subjected to action of a series of coherent high-frequency pulses that successively orient the total nuclear magnetic moment parallel and antiparallel to the x, y, and z axes in the RFC (so that its mean direction precisely corresponds to the angle θ_M). Consequently the dipole broadening is suppressed as far as second-order perturbations, which permits a resolution down to 10 Hz.[10,11]

Finally, "hybrid" methods have recently been proposed, which combine the high sensitivity characteristic of double resonance in an RFC with effective suppression of dipole-dipole broadening of lines[5] (one of the key reports at the Congress was devoted to this topic, which was presented by a group of collaborators at the Massachusetts Institute of Technology headed by J. Waugh). It is not necessary in this case to use the "magic angle," since the width of NMR lines of "rare" spins (S) mainly arises from the local magnetic fields of

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the "abundant" spins (I). For suppressing the former, it suffices continuously and rapidly to reorient the spins I by using a strong field at the resonance frequency ω_I. Application of these methods to ^{13}C nuclei (of natural abundance 1.1%) opens up broad prospects of studying the structure of chemical bonds in solid organic compounds.

We cannot but mention another recent study by Waugh's group, whose results have made a sort of sensation among the specialists.[12] By using a set of special high-frequency pulses, these authors have regenerated the transverse component of the nuclear magnetization of a solid (M_x) after it had vanished in the process of free transverse relaxation. In contrast to the ordinary "spin echo" effect, which is due to inhomogeneous broadening, this experiment was performed on a system having a homogeneous dipole width of NMR lines. As we know, the vanishing during transverse relaxation of the mean values of all observable quantities that have nondiagonal operators in the z-representation (including $\langle M_x \rangle$) permits us to speak of establishment of a canonical distribution characterized by a spin temperature.[3] By analogy with "ordinary" thermodynamics, this process has generally been considered irreversible. This has been refuted by brilliant experiments by Waugh's group. This result, paradoxical at first sight, demonstrates the very interesting features of spin systems, and it shows that, however useful the concept of the spin temperature is in describing a very large set of phenomena, it nevertheless does not always correspond to ordinary thermodynamic conceptions.

The fundamental conclusions of modern many-particle theory of spin systems, which have given such valuable practical results in NMR, have recently been transferred to electron spins and electron-nuclear interactions. One of the most interesting lines is represented here by studies on dynamic polarization of nuclear spins (DPN) in crystals having electronic paramagnetic impurities. In the last few years, the well-known "solid effect" (see, e.g.,[16]) has been supplemented by new DPN mechanisms based on energy exchange between the nuclear spins of the lattice and a reservoir of electronic dipole-dipole interactions of an impurity:[14] the role of spatial diffusion of the nuclear spin temperature has become much clearer.[15] Great advances have also been made in practically obtaining high nuclear polarization, with a fundamental field of application in polarized targets for use in elementary-particle physics. It has recently been possible to produce hydrocarbon targets having a proton polarization above 80% (see, e.g.[16]): there have been reports of approach of this quantity to 100%.

New, interesting ideas in this field have been realized by the group of A. Abragam (French Center of Nuclear Studies), who reported at the Congress the experimental detection of "nuclear pseudomagnetism."[17] The essence of the phenomenon is that, when the polarized protons of a target interact with neutrons striking it, the latter are acted on by the "pseudomagnetic field" of the protons. This field (it proved to be about 25 kOe) could be measured from the frequency shift of the neutron paramagnetic resonance. Here the high-frequency, high-amplitude field needed for detection of the latter was very ingeniously obtained by using the same proton pseudomagnetism, but now in a rotating frame. Along with a recent study of the same group on producing nuclear antiferromagnetism,[18] this important result demonstrates the variety of possible applications of polarized nuclear objects.

Application of the concept of spin temperature to EPR and ENDOR is now mainly being developed in the studies of the Leyden school (see, e.g.[19]) that were reported at the Congress in a review paper by W. Wenckebach and N. Poulis. This problem is elucidated in detail in the review.[20] However, we should note that the distinctive features of impurity electron spin systems (the essential role of inhomogeneous line broadening, large mean energies of dipole interactions, short lifetimes of transverse relaxation, etc) do not as yet allow us to transfer to EPR the elegant methods of NMR spectroscopy in rotating frames. Apparently this problem will be solved in the very near future.

Among the other current problems in the electron-resonance field, we should mention the study of mechanisms of spin-phonon interaction. In spite of the considerable number of studies and the appearance of new, original ideas (see, e.g.[21]), there is as yet no full clarity on the problem of the nature of concentration acceleration of electron spin-lattice relaxation in doped paramagnetic crystals. Apparently one of the pathways toward solving this problem (as well as a number of others) lies in using acoustic paramagnetic resonance, the theory and practice of which are now being intensively developed (see, e.g.,[22-24]). The method of Mandel'shtam-Brillouin light scattering (using a laser) has contributed greatly in studying spin-phonon interactions. It permits one directly to measure the spectrum of "hot" phonons that are formed by spin-lattice relaxation under "phonon bottleneck" conditions. In particular, this method has recently been used to detect a "phonon avalanche" effect (regenerative amplification of phonons of a certain frequency). This effect arises when the wings of an EPR line are saturated, and it involves a strong lowering of the spin temperature of the dipole-dipole interactions[25] (the paper by the group of physicists at Kazan' on this topic aroused great interest at the Congress).

Application of optical methods proves very fruitful also in other branches of EPR spectroscopy. Thus, general attention has been attracted recently to EPR studies on optically excited triplet states in molecular crystals, which give rich information on the structure of the energy spectrum of the triplets and of singlet-triplet interactions. In particular, these studies found a considerable deviation from an equilibrium distribution of spins over the magnetic sublevels of the excited triplet (the "optical electronic polarization" (OEP) effect[26]), and an inverted population was detected, which gave rise to induced emission in the UHF range. In a number of cases, the OEP effect is also accompanied by dynamic polarization of the protons in the crystal,[27] the mechanism of which is not yet fully clear.

There is no point in presenting here in detail the numerous (and often very useful) results of applying EPR, NQR, ENDOR, and other standard methods of radiospectroscopy to study structures, local symmetry, degree of covalence, and other parameters of various impurity centers and defects in crystals, since such studies are rather traditional. We note only that these methods have recently gained valuable information on the behavior of solids near phase-transition points (magnetic, electrical, and structural), including data on order parameters, rotation of atomic groups, fluctuation spectra, etc. (see, e.g.[28,29]). A new approach is to study similar phenomena in liquid crystals.[30] As we know, the latter play a large role in biologically important systems, and they have recently been applied more and more widely in technology (see, e.g.[31]).

New prospects are opened up by a recent method of paraelectric resonance (PER), which permits one to study spectra of impurity centers that have a permanent electric dipole moment (e.g., OH^-, Li^+, or Ag^+ in KCl) in the UHF region.[32] Splitting of the levels of the paraelectric center in the intracrystalline field is due to tunneling of the dipole moment among equivalent equilibrium orientations, and it is usually of the order of several cm^{-1}. An external electric field (or an elastic stress) shifts these levels, similarly to what happens in a paramagnetic material subjected to a magnetic field. PER spectra are distinguished by a considerable width of the resonance lines (10^8—10^{10} Hz). This is due to their high sensitivity to inhomogeneities of the intracrystalline field and to strong dipole-phonon coupling (see, e.g., [33]). The latter circumstance has recently been used successfully for generating and detecting UHF phonons.[34]

We note in conclusion that the rapid perfection of the methods of modern radiospectroscopy is based not only on advances in the theory, but also on marked elaboration and improvement of quality of the research apparatus. As a rule, the latter now include elements of computer technology, signal accumulators, Fourier transformers, etc.

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Elementary nonlinear optical phenomena

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A new line of research has taken form in recent years that lies at the boundary between nonlinear optics, atomic physics, quantum radiophysics, and plasma physics; this is the study of elementary nonlinear optical phenomena. Such phenomena (which take a high-intensity light field to observe) as the creation of electron pairs, the stimulated Compton effect, many-photon ionization and many-photon excitation of atoms, resonance dissociation of molecules, and the nonlinear surface photoeffect are not only of independent interest. On the one hand, study of these phenomena furthers the development of quantum electrodynamics and quantum mechanics. On the other hand, these phenomena are the basis of a number of astrophysical processes that occur when powerful laser radiation interacts with matter, of resonance chemistry, and of a number of new methods of plasma diagnostics.

The progress in development of lasers now permits us to get field intensities approaching atomic values over a broad range of wavelengths (from several hundred Ångströms to ten microns). Utilization of dye lasers has furnished experimenters with a source of intense light with smoothly variable frequency. Extremely high radiation intensities are attainable at a number of wavelengths. One can achieve the (currently) record-