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REVIEW

Celebration of 80 Years of EPR

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Abstract
We celebrate 80 years of EPR with a special issue of Applied Magnetic Resonance featuring both reviews and regular research articles. The focus is new opportunities for application of EPR and new directions for development of EPR. This introduction concisely surveys the scope of EPR and hints at future developments.

1 Overview

Unsuccessful efforts by Gorter to observe magnetic resonance were followed by success in gas-phase NMR by Rabi in 1938 [1], in condensed phase EPR at low frequencies by Zavoisky [2] in 1944, and then NMR in condensed phase by Purcell (solids) [3] and Bloch (liquids) and coworkers in 1946 [4]. Independently, the Bleaney lab began measuring energy level splittings in transition metals by EPR at several frequencies, including X-band [5]. Zavoisky's experiments were cited by Bleaney in the Bagguley and Griffiths announcement of X-band results [6]. Stimulated by Gorter, Zavoisky, and Purcell et al., Cummerow and Halliday [7] measured paramagnetic absorption of solid $MnSO_4 \cdot 4H_2O$ at 2.93 GHz. The instruments used by Zavoisky [8] and by Bleaney differ greatly, supporting claims of independent development. Although, Zavoisky was the first to observe resonance and the first to publish, Bleaney's approach was more widely adopted and subsequent EPR measurements were predominantly conducted in the X-band (ca. 9–10 GHz) region. The subsequent development of EPR illustrates strong interaction between selection of spin systems to study, development of instrumentation, and development of theory of spectra and relaxation times. Fundamental theory [9, 10] preceded the search for resonance [9–12]. The early history of EPR is well-documented in Kochelaev and Yablokov [13]. Much of the first 50 years of EPR effort was celebrated in

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Foundations of Modern EPR, edited by Kev Salikhov and Sandra and Gareth Eaton [14]. A relaxation perspective on the history is presented in [15].

Early papers reported observation of EPR signals from a wide range of paramagnetic species including transition metals, lanthanides, organic radicals, and defect centers in solids. The selection of paramagnetic species provided answers to many fundamental questions and supported interpretation in terms of nuclear hyperfine couplings, g-values, and anisotropy of each. The role of excited electronic states was revealed. EPR provided means of studying oxidation states and structures of transition-metal complexes and detailed electronic structure and motion of organic radicals. For example, the R_2NO moiety called nitroxide or nitroxyl was known before EPR was available to confirm the assignment as a free radical, and the initial spectra also confirmed the molecular orbital picture of bonding that predicted nitrogen nuclear hyperfine interaction. The chemical and biologic versatility of nitroxides contributes to a vast literature. The challenge to understand spin physics stimulated elegant mathematical simulations of spectra. The success at X-band and the predictions of theory guide major efforts to achieve greater sensitivity and expand to both higher and lower microwave frequency and magnetic field. Extremes of temperature, pressure, and other sample environments are goals of many research teams. In the first two decades many relaxation time measurements were made. The selection rules that fit these spectra and the interpretation in terms of the direct and Raman processes and then with the addition of the Aminov-Orbach process became the basis for textbook introductions. More recently, there has been more focus on exceptions to the simple arguments and effort to understand the mechanisms of relaxation.

EPR is a vast field. We have endeavored to reflect its depth and breadth, but it is impossible to be comprehensive. Readers may favor papers other than the sampling that we cited. A small sampling of published papers that illustrate the wide scope of EPR is presented in this introductory review. The emphasis is on papers that point to opportunities for future explorations, but to provide a balanced perspective of foundations and applications of EPR a few papers that reflect current mainstream topics are also mentioned.

2 Monographs

Several monographs produced after about 2 decades of development of EPR brought important features of EPR to the scientific community. Assenheim provided an introduction to EPR [16], Wilmshurst to the spectrometers [17], while Orton focused on transition metals [18] and Lancaster on semiconductors [19]. Ingram's [20]and Swartz et al. monographs [21] emphasized biologic and biochemical applications. The extensive multivolume series of books edited by Lawrence Berliner highlighted biologic applications of EPR. Textbooks such as Al'tschuler and Kozyrev [22, 23], Wertz and Bolton [24] and Atherton [25] were crucial to expanding the community of scientists that could apply EPR to solving problems. After the Eatons demonstrated the conditions needed to perform CW EPR quantitatively, their Quantitative EPR book became an important introductory text [26]. Research monographs such as Abragam and Bleaney [27], Standley and Vaughan [28], and Schweiger and

Jeschke [29] are foundations on which modern EPR is based. Modern research is also enriched by the monographs by Brustolon and Giamello [30] and by Goldfarb and Stoll [31]. The "bible" for EPR instrumentation and methodology has been Poole's 1967 monograph [32], with a second edition [33], and expanded in two volumes of a Handbook of Electron Spin Resonance [34, 35].

Readers are urged to consult standard textbooks [27, 29, 30, 32, 33, 36–38] and recent monographs [31, 39, 40] and many of the reviews in Berliner's Biological Magnetic Resonance series [41] for background omitted from this brief survey.

3 Instrumentation

Pictures of the Zavoisky spectrometer are of a reconstruction in the Zavoisky museum (http://chiralqubit.eu/a-visit-to-the-Zavoisky-museum) in Kazan, based on his lab notebooks [8]. Although the introduction to EPR of the lumped circuit loop-gap resonator by Hyde and Froncisz [42] revolutionized many applications of EPR, it had been forgotten that Zavoisky's original EPR resonator was a loop-gap resonator.

Key instrumental developments were high-Q reflection cavity, magic T and then circulator, low-noise Klystron (now replaced by low-noise Gunn diode sources), reference arm, magnetic field modulation and lock-in detection, high homogeneity magnets with high-stability power supplies, Hall-probe feedback magnetic field control, and solid-state electronics. In modern spectrometers all operations are under computer control.

For many years EPR measurement was predominantly continuous wave (CW) and predominantly X-band (ca. 9–10 GHz). Two types of pulsed EPR were developed, which have become known as saturation recovery and spin echo. Instruments capable of these pulse experiments were all home-built until Bruker developed the ESP380 FT-EPR spectrometer in 1987. The development of pulse methods has played a major role in the development of EPR spectroscopy and its applications. In the early stages, in the 1960s and 70s, the main driving force was Mims in the U.S. [43] and the Milov, Raitsimring, Salikhov, Tsvetkov, and Yudanov team in Novosibirsk [36]. The triumph of the spin echo method is that it overcomes the masking effect of the inhomogeneous broadening of the EPR spectra and facilitates identifying weak spin interactions. One of the remarkable achievements is the development of nanometrology based on the modulation of the observed electron-spin-echo signal caused by the dipole–dipole interaction between the spins of unpaired electrons [44–46] or between unpaired electrons and nuclei [29, 36, 43, 47, 48].

More recently, rapid scan EPR has become the third fundamental method of performing EPR [49]. Rapid scan does away with magnetic field modulation and lock-in detection. For long relaxation times and narrow spin packets, the magnetic field passes through resonance at times short relative to relaxation times. The time on resonance at constant microwave power is similar to the high-power-on time of pulsed EPR, so much higher power can be used with rapid scan EPR resulting in higher signal-to-noise relative to CW EPR. Duty cycle limitations of pulsed EPR usually result in rapid scan EPR providing better signal-to-noise per unit experiment time than pulsed EPR for species for which relaxation times are long enough to record spin echo spectra.

X-band resonators were initially transmission, but quickly evolved into the now-common reflection resonator. At X-band a rectangular cavity resonator became standard. The use of lumped circuit resonators facilitated extension of EPR spectrometers to both lower and higher frequency/field than X-band. An historical sidenote on this history is intriguing: A textbook attempting to persuade students about cavity resonators, started with a lumped circuit inductor and capacitor (a loop-gap resonator) and stepwise transformed it into a cavity. Several implementations of lumped circuit resonators show potential for optimizing particular applications of EPR. In addition to the loop-gap resonator (LGR), the Alderman-Grant resonator initially developed for NMR has been useful in low-frequency imaging [50]. Surface coils and implanted coils are being used in physiologic monitoring [51]. Parallel transmission lines, spiral coils, superconducting coils [52], and Ω-shaped microcoils [53] are being designed for measuring very small samples.

Frequency-tunable EPR spectrometers in the millimeter and submillimeter ranges have significantly expanded the capabilities of EPR spectroscopy. In the early 90s, such EPR spectrometer was created at Zavoisky physical-technical institute, the operating frequency of which can be smoothly adjusted in frequency in the range of 64–535 GHz [54, 55]. Subsequently, the frequency range was expanded to 37–1200 GHz. This made it possible to effectively use the spectrometer to study resonant transitions of non-Kramer ions (ions with integer spin) with singlet electronic states, the splitting between which lies in the operating frequency range of the spectrometer. The ability to operate in a wide frequency range distinguishes this spectrometer from most other high-frequency EPR spectrometers operating at fixed frequencies. It is important that the spectrometer makes it possible to directly measure the energy of excited electronic levels in a zero magnetic field. Many other high-field/high-frequency EPR spectrometers have been designed to explore spin systems that cannot be studied at the more common X-band and Q-band frequencies.

EPR instrumentation, commercial or locally built, now encompasses CW, rapid scan and pulse, zero-field to tens of tesla, low RF frequencies to teraHz, and microscopy to in vivo imaging and spectroscopy. Insights from high-field magnetic resonance stimulated major labs in several countries. Ohta and colleagues in Japan push the technological limits of multi-extreme EPR at high frequencies, high magnetic fields, and high pressures [56–58]. Benchtop size X-band spectrometers are available from several vendors, making X-band CW EPR accessible to a wide range of users. However, in spite of the many applications of EPR, the cost of most EPR instrumentation has limited acquisition by many laboratories and small sales volume has restrained investment in new spectroscopic capabilities.

4 Relaxation

It is fundamental to our understanding of spin relaxation, which underlies every application of EPR mentioned in this introduction, that electron spin angular momentum can couple to the lattice (T_1) only by interacting with some other angular momentum [27, 59–61]. Some angular momenta are measured by the g value, and a correlation is that the larger the g value difference from the free-electron g value the shorter the relaxation time. Relaxation in fluid solution results in part from coupling of the orbital angular momenta of the molecule with the rotational angular momenta of the molecule (the spin-rotational relaxation mechanism) [59, 62].

Attempts to understand electron spin relaxation began long before the observation of the electron paramagnetic resonance (EPR) phenomenon, and even before the recognition of electron spin. EPR was developed as a means of measuring electron spin relaxation times. Theories of spin relaxation developed prior to the discovery of EPR described spins in a crystalline lattice [10, 27, 28]. Consequently, many of the early applications, following the Zavoisky demonstration of resonance in liquid solutions, were of metal ions in crystals, either as pure compounds or diluted in a diamagnetic host. Since theories of 3d transition metals were most fully developed, and lanthanides were of intense interest, hundreds of these samples were measured in the first few years, especially by the Oxford lab of Bleaney [63, 64].

Since the magnetization, M, is proportional to the magnetic field, B, $M=\chi_0 B$, how does M change when B changes? That is, what is the mechanism of magnetic relaxation? Eventually, EPR makes it possible to study small numbers of discrete spin systems, but originally, the focus was on bulk solid samples. There were many experiments, especially by the Dutch group [65]. In parallel with the work on magnetism of solids, there were attempts to understand electronic spectra of gas-phase species, such as hydrogen. These concepts led to the idea that magnetic relaxation involved transitions between quantized electron spin energy levels. Early attempts to observe EPR were to understand spin relaxation [15]. Almost all advances in EPR technology have been based on the understanding of spin relaxation at the time, and facilitated further understanding. Now, we have three regimes of EPR, continuous wave (CW), rapid scan, and pulse. Each drives, and is driven by, our understanding of spin relaxation. Each of the more than 100 EPR experiment types exploit understanding of spin relaxation.

5 Transitions Observed

Magnetic dipole transitions are the basis for all common EPR measurements, but there may be cases in which the observations are not well-described by the textbook magnetic field B_1 perpendicular to the external magnetic field: $B_1 \perp B_0$ or $B_1 \parallel B_0$. Introductions to EPR describe selection rules that odd-spin systems (called Kramers species) will exhibit EPR spectra when $B_1 \perp B_0$ and even-spin systems (called non-Kramers) will exhibit EPR spectra when $B_1 \parallel B_0$. Some “dual mode” resonators (e.g., Varian E236 and Bruker ER4116DM) facilitate both types of measurements [66]. Extensive studies of parallel mode spectra have been performed on even-spin systems by Hendrich and coworkers [67]. Parallel mode spectra are weak relative to perpendicular mode spectra. The separation is not perfect, and both parallel mode and perpendicular mode spectra are observed in standard test spectra. We could expect that some spectra that should be observed in parallel mode would also be observed (weakly) in perpendicular mode [66, 68, 69].

It is commonly assumed that in spectrometers designed to excite spins with the magnetic field B_1 ⊥ to the applied magnetic field the signal is due to magnetic dipole transitions. We know, however, that each sample of finite size interacts with both the magnetic and electric fields of the microwaves. The interaction with the electric field is what causes some samples (described as lossy) to lower the Q of the resonator. Given that the sample is interacting with the electric field, it is reasonable to ask whether some of the observed spectra might be electric dipole transitions. Electric quadrupole transitions can also contribute [70].

Given the echo-detected and CW spectra obtained for Tb^{3+} and Tm^{3+} [68, 69], the question arises why do we observe any signal for the non-Kramers ions for $B_1 \perp B_0$? The echo intensities for these ions are about two orders of magnitude smaller than for the Kramer's ions, consistent with greatly reduced transition probabilities. Searching the literature for observations in other labs, we found that there were prior measurements for non-Kramer's ions with $B_1 \perp B_0$ but that in most of these papers efforts were made to rationalize the observation by suggesting that the B_1 ⊥ and $B_1 \parallel B_0$ separation is not good because of limitations of the resonator [71, 72]. However, the differences between spectra in the parallel and perpendicular modes suggest that different signals are observed in the two modes which may not be consistent with imperfect separation of modes. Other papers show fairly convincingly that the assumption that the transitions are magnetic dipole is not fully valid and electric dipole transitions contribute to the spectra [73–80]. Stronger spectra were observed when the sample was positioned in stronger electric field region of the resonator than in the magnetic field region. These B/E separations also are not fully achieved in resonators. Another contributing factor is that the nuclear hyperfine, although not resolved in the glassy spectra, is not in the high field limit [81–84]. There also may be extensive mixing of closely spaced energy levels. Hence, the explanation for the intensities of lanthanide EPR spectra remain incompletely demonstrated, but the spectra available so far clearly demonstrate that the "textbook" selection rules are not absolute.

6 Spin–Spin Interactions

Interactions between spins monitored by EPR inform us about many phenomena. Dipolar interactions between pairs of electron spins native or labeled in polymers, especially biomolecules, has become a major application of EPR. Interaction of electron spins with other electron spins and with nuclear spins yield hyperfine structure in EPR spectra, but not all such couplings are resolved. Multiple resonance techniques for sorting out spin–spin interactions were reviewed by Dorio and Freed [85]. Important information about nuclear couplings too small to cause resolved hyperfine lines can be obtained by the ENDOR method [86–88]. Combined electron and nuclear resonance techniques, and photoexcitation, have constituted the majority of reports of extensions of EPR beyond just electron spin transitions [89]. The observation of nuclear spin modulation in EPR spin echo decay patterns (called ESEEM) very usefully reports the environment of the electron spin [48]. After demonstration by Mims [43] and extensive elaboration by Kevan and coworkers a 2D version (HYSCORE) was developed by Höfer [48, 90]. Recent extensions include the electric vector of laser excitation [91].

ENDOR, DEER, and many other multiple resonance techniques have opened new vistas in science. It has been known for a long time that dipolar interactions between unpaired electrons contain distance information. This information was extracted from spectral shapes, intensities of half-field transitions, relaxation times, and other phenomena. The demonstration that free radicals could be attached at defined locations in polymers and especially in proteins and nucleic acids created a vigorous field of exploration of spin–spin distance measurement, known as DEER [92], pulse dipolar spectroscopy and a few other such terms. Until recently, most DEER studies applied nitroxide spin labels. Other labels, ranging from trityl radicals [93] and Gd^{3+} complexes [94] to copper complexes [95] show the advantages for some applications of exploiting particular features of previously unused spin systems.

Recently Salikhov formulated a new paradigm of electron–electron spin exchange and its manifestations in EPR spectra shape which gave a good impetus to the development of the theory of paramagnetic relaxation in solutions and the application of EPR in physics, molecular biology, etc. [96]. The main theoretical provisions of the new spin exchange paradigm [38, 97–104] have been confirmed experimentally [105–111].

7 Extremes

7.1 Smallest Number of Spins Detected

Commercial X-band EPR spectrometers can detect about 10^9 spins under defined conditions [26]. This could be improved a factor of two or so by decreasing losses in the signal detection pathway in special cases. Blank and coworkers [112, 113] demonstrated induction–detection sensitivity down to a few tens of spins in very small resonators and compared induction–detection to other methods of detecting electron spins. Increased sensitivity provides opportunities to solve new problems. Drost et al. [114] combined EPR with scanning tunneling microscopy. Better signal-to-noise will be a central focus of EPR development. Various methods of atomic microscopy or micro-resonators are exploited to see how few spins can be detected. With a 7.3 GHz micro-resonator at 1.2 mK a spin echo measurement detected 65 spins of bismuth donors in silicon [115]. Single spin observation is probably not possible with induction spectroscopy [116] but force microscopy methods combined with ODMR look promising for NV centers in diamonds. ODMR of triplet radicals allows Hahn echo formation because the detection time of the ODMR signal is very long relative to spectral diffusion time within the spin system. The result is a temporal rather than a ensemble average[117]. ODMR evolved from the study of triplet states by Hutchison and Magnum [118] and van der Waals and de Groot [119]. Since then there is a large literature of EPR of triplet states [120, 121], including in photosynthesis [122].

Some studies of very low concentrations of spins show spectra that have the shapes recognizable from studies at the usual concentrations. As the spin concentration is lowered, the recognizable spectra shape are due to long-time signal averaging. Long-time here means relative to all of the relaxation times. If one were to observe the spectrum due to a countable number of spins in a single scan, the spectrum should exhibit just the number of sharp lines due to whatever combination of molecular orientations and nuclear spin states happened to exist at the moment of resonance. There will be interesting possibilities for deviations from the normal expectation that the ensemble average will equal the time average.

7.2 Largest Sample Studied

Reversing the focus on the smallest number of spins, which often involves study of a very small sample, we now ask what is the largest sample studied? In NMR the largest sample is not the horse in the MRI but rather the rock formations outside the bore-hole when drilling for oil, etc. So far the largest samples studied by EPR are pieces of artwork and sculptures seeking the nature of the materials, the source of marble [123], and in vivo studies of animals and people, using surface coil resonators [124–127].

7.3 Lowest Frequency and Highest Frequency

Very low magnetic field/frequency and very high magnetic field/frequency studies reveal aspects of EPR spectra that cannot be measured at the more common X-band and Q-band frequencies. EPR observed at zero magnetic field by using swept RF/microwave frequency yield improved spin Hamiltonian parameters [128]. Forbidden transitions are much more intense relative to allowed transitions at low field and 8 transitions can be observed for nitroxide radicals in dilute fluid solution [129]. Small g value differences are better defined the higher the field. Some transitions are at high enough energy that they can be observed only at high magnetic field and high microwave frequency.

Frequency dependence of sensitivity depends on the sample size. For a very small (almost a point) sample the sensitivity increases as $\omega^{11/4}$ if the resonator size decreases as $1/\omega$. If both the sample size and the resonator size can increase as $1/\omega$, then the sensitivity increases as $\omega^{-1/4}$ [130]. These predictions depend on constant noise figure of the spectrometer detection system. In very few cases has this been achieved. Especially for very high-frequency measurements the sensitivities have not improved as predicted because the spectrometer design focused on observation at a particular high field/frequency of a strong signal, not optimization of the signal detection path. The work of Graham Smith in St. Andrews has guided spectrometer design at 95 GHz [131].

Insights from high-field magnetic resonance stimulated major labs in several countries. Ohta and colleagues in Japan push the technological limits of multi-extreme EPR at high frequencies, high magnetic fields, and high pressures [56–58]. Persistent superconducting magnets provide opportunities for up to THz EPR in some labs [58, 132–135]. In somewhat of a reversal, EPR of a known sample such as DPPH has been used to measure very high magnetic fields. Observation of the

EPR signal proves that the high field was achieved. Commercial EPR spectrometers are available at 263 GHz.

7.4 Smallest Spectrometer

Traditional X-band and higher frequency spectrometers with iron-core electromagnet or superconducting magnet, console, temperature control systems, etc. occupy significant floor space. Bruker has been marketing progressively smaller benchtop X-band spectrometers, and some research labs have developed purpose-built small spectrometers including a hand-held magnet-based spectrometer [127], a benchtop 700 MHz imager [136], and an EPR mouse [137]. There is increasing interest in applications of an "EPR on a chip" [138].

7.5 Extremes of Linewidths

One measure of performance of a spectrometer is the minimum line width and spectral resolution achievable with samples of various sizes. The usual magnet specification for a large electromagnet is 50 mG in a 10 mm diameter volume. With a small sample less than 20 mG linewidth can be measured. As pointed out in the Quantitative EPR book, a strong narrow signal, such as a LiPc particle, can cause the AFC system to overload yielding an artifact that looks like an even narrower spectrum. With increasing focus on long T_2 samples for applications such as quantum computing high resolution will be of increasing interest.

Some EPR spectra are so broad that they cannot be fully recorded within the limits of electromagnets. Scanning a superconducting magnet to observe the full spectrum would boil off a lot of helium. In some cases the theoretical g value is zero, so there is no limit to the magnetic field needed. This occurs in the lanthanides, the study of which excited early applications of EPR and now because of many applications of lanthanides in energy production is of increasing interest.

7.6 High-Pressure Liquid and Solid Samples

Changing the pressure on a sample provides important information about contacts between and among molecular species. It is very challenging to submit a sample to very high pressures, and especially in an EPR resonator where the materials have to have minimal interaction with the microwave field. Pressure dependence of biomolecular reactions can be studied using the device developed by Hubbell and coworkers [139]. Very high pressures (as high as 2.5 GPa) were achieved by Ohta and coworkers, and the g values of Co^{2+} in Tutton salt were shown to be pressure dependent[140, 141].

7.7 Low Temperature, High Temperature

Relaxation times are so fast for some metals that temperatures below 4.2 K are needed. Many such studies helped define relaxation by the direct process [28].

Low-temperature studies can show depopulation of low-lying states, and for example, quenching spin decoherence [142]. Very high temperatures needed to create some radicals require special resonator design to be able to heat the sample without destroying the resonator.

8 Sample Types

The typical paramagnetic species studied has evolved with the capabilities of spectrometers and understanding and ability to simulate spectra. Early EPR studies answered questions about spin states, nuclear spin values, and electron spin distributions in organic molecules, to cite a few examples. Certain radicals have proven to be particularly useful, or challenging. Nitroxides and triarylmethyl radicals (often called trityl) have almost endless applications to structure and function of biomolecules, in vivo imaging, and recently even batteries.

Collisions between species in the gas phase broaden EPR spectra, so most gas-phase studies of radicals are performed at lowered pressure. High-resolution spectra have been obtained for most paramagnetic 2- and 3-atom molecules. A few studies have been made of nitroxides in supercritical fluids [143, 144]. The bistrifluoromethyl nitroxide was studied by Schaafsma and Kivelson [145]. Kinetics of gas-phase radicals was summarized by Westenberg [146]. Spectra of O_2 sharpen at low pressure. The atmosphere above a liquid or solid sample from which O_2 was incompletely removed can contain multiple lines due to O_2 [147]. Batchelor [148] reported gas-phase EPR of three nitroxides, five carbon-centered radicals, and one oxyaminyl radical.

Due to the anisotropy of g and hyperfine values, many dynamic studies can be performed with temperature and/or solvent viscosity dependence of CW lineshape. Nitroxide radicals monitored with CW and pulsed EPR has taught the world of science more about motion in solution than any other technique [149]. Time dependence of EPR amplitudes reveals kinetics from as long as one can monitor to as fast as samples can be mixed. Mixing flowing liquids and getting the solution to the active region of the resonator achieves sub-millisecond time scales [150]. The new rapid scan technique [151] also facilitates kinetics studies limited only by the ability to detect the needed signal during each pass of the field through resonance. Exploration of this technique has only begun.

Photosynthesis poses almost limitless questions for EPR to answer. Nearly the full extent of EPR spectroscopy has been applied to understanding photosynthesis. The book by Mobius and Giacometti [152] provides an overall perspective on photosynthesis. Reviews of specific areas include electron transfer [153] and high-field EPR [154]. Much of what is known about the bacterial reaction center structure and function was learned via EPR measurements.

Building on the background understanding of common-studied elements like V, Cr, Mn, Fe, and Cu EPR is increasingly used to determine oxidation states, coordination environments, etc., of less-familiar elements. The spectra of Mn^{2+} would be familiar to most readers of this survey, but EPR is important for demonstrating the presence of $3d^1$ Mn^{6+}, manganate, in various materials [155]. Similarly, Cr^{3+} is the most commonly studied oxidation state of Cr, but 3d^1 Cr^{5+} with its long relaxation times is easily studied by EPR. Oxidation states that yield even-spin states are usually best studied with parallel mode EPR, but some have also been studied in the normal perpendicular mode [68, 69]. Bismuth radicals were studied by Haak et al. [84].

8.1 Active Centers of Solid-State Lasers

Van Vleck extended his theory of paramagnetic relaxation [156] to metals in solid-state materials at conferences on quantum electronics in 1959 and 1961 [157, 158]. Impurity crystal lasers find numerous applications in industry, medicine, scientific research, etc. One of the most important conditions for their successful operation is the quality of the crystals used. The analysis of EPR spectra makes it possible to determine the microenvironment of the active impurity, evaluate the quality of the grown crystal, and identify undesirable, i.e., uncontrolled, ions. In the years since the discovery of EPR, scientists from different countries have accumulated extensive experience in studying crystals with paramagnetic impurities. A large class of various laser materials has been studied. The first solid-state laser based on the laser properties of impurity ions in crystals was created in [159]. The active center in this laser was trivalent chromium (Cr^{3+}) in ruby (Al_2O_3). Since then, laser generation of chromium ions embedded in other crystal matrices, in particular, in synthetic forsterite (Mg_2SiO_4), has been obtained. In this crystal, laser generation, tunable in the wavelength range of 1.130–1.320 microns, was obtained on tetravalent chromium ions [160]. With forsterite crystals doped with chromium and lithium, laser generation of trivalent chromium ions in the wavelength range of 1.030–1.180 microns was obtained [161–163]. A series of studies of dimeric associates of non-chromeric rare earth ions in oxide crystals have been reported [55, 164–166].

8.2 Spin Clusters

Particular interest in spin clusters is associated with the discovery of molecular clusters with memory effect, the so-called single molecular magnets, SMM. The first and most famous SMM is built from 12 Mn ions [167]. In the study of such multicore clusters, high-field multi-frequency EPR spectroscopy is used, which even in the case of a twelve-core cluster $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ $2CH_3COOH4H_2O$ and the ground state with $S=10$ allows us to obtain important information about the anisotropy of the magnetic properties of this cluster [168, 169]. Intense current interest to construct new SMMs with higher blocking temperatures tends to be focused on mixed-metal systems containing both lanthanide and transition-metal ions [170–172].

9 Imaging Physiology

The development of nuclear magnetic resonance imaging stimulated analogous development in EPR, but the differences in spin concentrations and relaxation times required different technologies. Initial experiments were performed independently and essentially simultaneously in three labs [173]. Early imaging used mostly solid materials with single X-band EPR lines. The development of spectral-spatial imaging [174, 175] demonstrated that varying spectral line shapes could be monitored throughout a heterogeneous sample. In vivo imaging required lower microwave frequencies and lower magnetic fields [176–179]. Many of the studies used nitroxide radicals. When triarylmethyl radicals of long-time persistence in vivo became available, their greater sensitivity to collisions with O_2 relative to nitroxides opened new horizons in EPR oximetry [180]. Both localized spectroscopy and multidimensional imaging contribute importantly to preclinical physiologic studies. The labs of Halpern [181, 182], Krishna [183], Swartz [184], Gallez [185, 186], Utsumi [187], Hirata [188], Blank [189], and others combine EPR spectroscopy and in vivo imaging to monitor animal and human physiology, with a strong focus on O_2 concentrations in tissue [179, 177, 178].

10 Dosimetry

Defects created by ionizing radiation yield characteristic EPR signals. Many of the defects are persistent at room temperature, quantitatively related to the incident radiation, and useful for dosimetry and dating archeologic sites. Radiation-induced defect sites in teeth are especially long-lived. Since teeth are among the best-preserved items in ancient sites, EPR is an important tool for dating archeologic sites [190]. Radiation from radioactive elements in the dirt surrounding teeth and other objects to be dated create defect centers whose intensity is an integration of the exposure time. The primary uncertainty is whether the object has relocated over the ages so that the radioactivity of the current environment is not representative of the entire period during which it was buried. The defects in irradiated alanine have been characterized extensively and alanine is widely used as a quantitative dosimeter [191]. Alternative materials with simpler or more intense spectra are a focus on current research. Irradiation of foodstuffs to keep it fresh longer produces defect centers in bone or carbonaceous portions, with radical lifetimes that are longer the drier the material [192–194]. Although it might not be very appetizing to consider, quartz grains in the dirt accompanying fruit and vegetables are good reporters of radiation. In the case of accidental radiation exposure, EPR can provide a clinically useful measure of the magnitude of the radiation dose [195].

11 Applications

Photogenerated radicals provided fundamental understanding of photographic film, and now guides development of solar energy conversion materials. EPR signals of petroleum, damage to lubricating fluids, and monitors of whether shipments of materials across national borders were irradiated have dominated industrial applications of EPR. In addition to the industrial food treatment mentioned above, in the past couple of decades, free radical tests that predict the shelf-life of beer, vegetable oils, etc. have expanded the applications of EPR. Looking to the future, the unique spectra of labels that can be added to accompany products could track products through commerce and reveal counterfeits.

Pigments have characteristic EPR signals from the metals that they are made of. For example, a blue pigment might be a copper salt, or it might be lapis lazuli, which contains S_3^- radical. The fine limestones chosen by sculpturers have characteristic signals that in some cases permit identifying the quarry from which the stone came [123].

12 Computations

Spin distributions in organic molecules can be calculated fairly well by modern molecular orbital programs such as ORCA and Gaussian and many others. The rest of the periodic table remains a challenge that many research groups are undertaking. One can anticipate major advances in spin distribution computation, especially for $S > ½$. The EasySpin shareware software makes simulations of EPR spectra for a wide range of species widely accessible [196].

Early relaxation measurements led to understanding of relaxation in terms of direct, Raman, and Orbach-Aminov processes [28]. As is emphasized in [59] the temperature dependence of the processes tell us little about the mechanisms of relaxation. Most recent studies seek to understand the mechanisms of relaxation. Advances in computation capabilities now permit attempts to include vibrations at the molecular level, explicit excited states, details of methyl rotations, etc. [197, 198]. This is a new field of computational EPR that as it evolves could guide selection of molecules designed to have specified relaxation properties.

13 Future Directions

From its beginning EPR has given new purpose to technology developed for some other application. Recently we have seen the utility of arbitrary waveform generators and newly developed GaN amplifiers. EPR will benefit from many aspects of new developments in communications such as software-defined radio, miniaturization of components, and the like.

Some EPR spectra can be observed only at cryogenic temperatures. Early studies inserted resonators and sample in Dewars containing liquid N_2, liquid H_2, or liquid He. The flow cryostats developed for commercial EPR spectrometers expanded the range of temperatures available, which was especially important for relaxation studies. The scarcity (and high cost) of liquid He limited these EPR studies. Recent development of closed cycle He cooling systems designed to be used with EPR spectrometers facilitate more extensive use of temperatures below those accessible with liquid N_2 (see, for example, [68]).

Machine learning and artificial intelligence have become terms of popular culture as this is being written. The current technology uses the prior knowledge that is in the available data base, so it is biased toward correlations and extrapolations of that prior knowledge. The power of this is simply that the scope of the prior knowledge is beyond the capabilities of most people to put together coherently. However, because of the limitations of the data base, one hopes that most scientists will be able to test correlations and predictions against what they know well in their field and determine whether it makes sense. Extensive knowledge of "what is in the box" has been the basis of creativity in the past. The evolving computer-based new tools can extend the capabilities of scientists but have to be used with insight.

Current research will lead the way to quantum computing, quantum informatics [199–206] and health applications in the clinic [98, 199]. New ways of manipulating spins will uncover new vistas. Much has been learned and applied, but there are vast vistas beyond our current ability to see. The future is limited only by the imagination of the next generation of students.

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Declarations

Conflict of Interest The authors declare no competing interests.

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