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Using EPR spectroscopy to go from the Jahn–Teller effect to nuclear waste disposal

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Abstract

Electron paramagnetic resonance (EPR) spectroscopy is a powerful technique for elucidating the fundamental solid-state-chemical and crystal-field ground-state electronic properties of rare-earth and actinide ions that are incorporated into single-crystal host materials. In the case of rare-earth or rare-earth-like ions that are characterized by a degenerate orbital doublet ground state when placed in a cubic crystal field, EPR has proven to be an extremely valuable approach to the study of various manifestations of the Jahn–Teller (J–T) effect. The contributions of EPR spectroscopy to the study of the J–T effect in ions such as La^{2+} , Y^{2+} and Sc^{2+} include the discovery of quadrupolar effects in J–T systems and a verification of Frank Ham's theory of the dynamic J–T effect. Such basic studies can often have unforeseen consequences—like leading to the discovery of new scintillators for gamma-ray detection or the development of a matrix for the disposal of radioactive waste.

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1. Introduction

The privilege of being able to carry out basic and applied research on the fascinating properties of the rare earths and actinides since my 1966 “initiation” into this field is enhanced to the extreme by my receipt of the 10th Frank H. Spedding Award. The opportunity to work on so many fascinating and diverse problems, to interact with so many talented collaborators, and on all-too-rare occasions, to be able to discover something new or to solve some really tough problem would have been reward enough. The honor of receiving the Spedding Award, however, provides a capstone that is particularly meaningful to me since this recognition comes from other researchers and colleagues—from scientists who have also known long days and nights spent in the laboratory or laboring over calculations, from scientists who have also felt the sting of failure and known the frustration of having to start all over.

In addition to no small measure of personal satisfaction, this fortunate event provides me with a retrospective opportunity to recognize the contributions of a

number of collaborators, advisors, and colleagues with whom I have had (and in some cases, still have) the pleasure of interacting. My personal “introduction” to the rare earths came while I was a graduate student in the Physics Department at Vanderbilt University. After a year of fruitlessly pursuing an electron-paramagnetic-resonance (EPR)-based dissertation problem of my own choosing, I had the good fortune in 1964 to visit the Solid State Division at Oak Ridge National Laboratory in Oak Ridge, TN. There I met Marvin M. Abraham, an experienced and highly accomplished EPR spectroscopist in the field of rare-earth and actinide ions. He quickly pointed out why my “personally generated” thesis concept that I had so diligently pursued for over a year was effectively nonsense and was never going to work. Following this devastating realization, I would have been at a total loss as to how to proceed without the timely intervention and assistance of Marvin Abraham and his help in identifying a tractable dissertation problem.

During the time period of the 1960s and extending into the mid 70s there was a considerable and widespread level of interest in the subject of the crystal-field splitting of the ground state of rare-earth ions with half-filled shells (so-called S-state ions). It was in this area of

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rare-earth research that Abraham laid out a course of experiments for me to undertake as a thesis subject. The basis of the problem was (and still is) that for the f^7 electronic configuration of the rare-earth ions Eu^{2+} , Gd^{3+} , and Tb^{4+} the Hund's rule ground state is $^8S_{7/2}$. When ions with a pure $^8S_{7/2}$ ground state are incorporated as a substitutional impurity in a host crystal, a first-order calculation of the interaction between the crystalline electric field (CEF) and the S ground state yields a null result—regardless of the symmetry of the crystal field. Experimentally, however, a splitting of the $^8S_{7/2}$ ground state by the CEF is observed—leading directly to the problem of identifying the mechanisms that are responsible for the observed effects. A variety of higher-order interactions and mechanisms were being (and have subsequently been) considered as the source of the CEF splitting of S-state ions. For example, the ground state of the rare-earth S-state ions is not strictly pure $^8S_{7/2}$ due to the admixture of other levels by intermediate-coupling effects. (Such effects are even more significant in the case of the analog S-state actinide ions Am^{2+} , Cm^{3+} , and Bk^{4+} .) Various early attempts to account for the observed CEF splitting of S states had involved calculations based on different combinations of spin–spin, spin–orbit, orbit–lattice, etc. interactions, and these attempts were not successful. This lack of success in the theory area provided the motivation for obtaining more systematic experimental data related to the interactions between crystal fields and S ground states. Accordingly, the thesis topic that Marvin Abraham identified for me was directed toward the experimental avenue of trying to solve or contribute to the solution of

the problem of explaining the crystal-field splitting of the ground S state of rare-earth ions.

In a fortunate combination of circumstances, at the time of my visit to the Oak Ridge National Laboratory (ORNL), high-quality, rare-earth-doped single crystals of the cubic fluorite-structure materials CeO_2 and ThO_2 were being grown at ORNL by an outstanding crystal grower named Cabell Finch. Abraham and Finch were collaborating on studies of these and similar rare-earth-doped materials, and I was offered the opportunity of carrying out EPR experiments on CeO_2 and ThO_2 crystals that had been doped with Gd^{3+} for my thesis problem. This opportunity initiated an effectively continuous collaboration involving EPR and other studies of rare-earth, actinide, iron group and other ions that lasted from 1964 until Abraham's retirement from the ORNL Solid State Division in 1994. The results of this long-term collaboration are documented in a number of publications [1–90].

Armed with the Gd-doped cerium and thorium oxide single crystals, I returned to the Physics Department at Vanderbilt and was able to immediately begin to make progress. The popularity of using EPR spectroscopy to studying S-state ions during this time period was not only due to interest in resolving the basic scientific issue noted above, but also to the fact that these ions can be readily investigated at room temperature—unlike the other rare-earth ions that generally require near-liquid-helium temperatures for their observation using EPR. We had no cryogenic capability on our EPR spectrometer at Vanderbilt; so the $\text{CeO}_2:\text{Gd}$ and $\text{ThO}_2:\text{Gd}$ systems were ideal subjects for me to investigate. Fig. 1

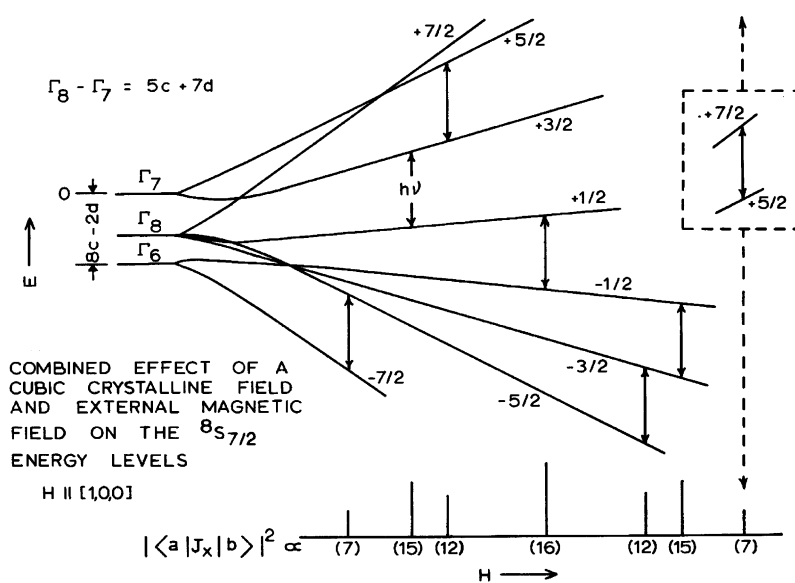


Fig. 1. Energy level diagram showing the energy levels resulting from the effect of the splitting of an $^8S_{7/2}$ state by a cubic crystal field. The final degeneracy of the system is removed by the application of a dc magnetic field to produce the eight energy levels indicated. EPR transitions between the levels are shown along with an idealized 'stick' EPR spectrum at the bottom of the figure [92].

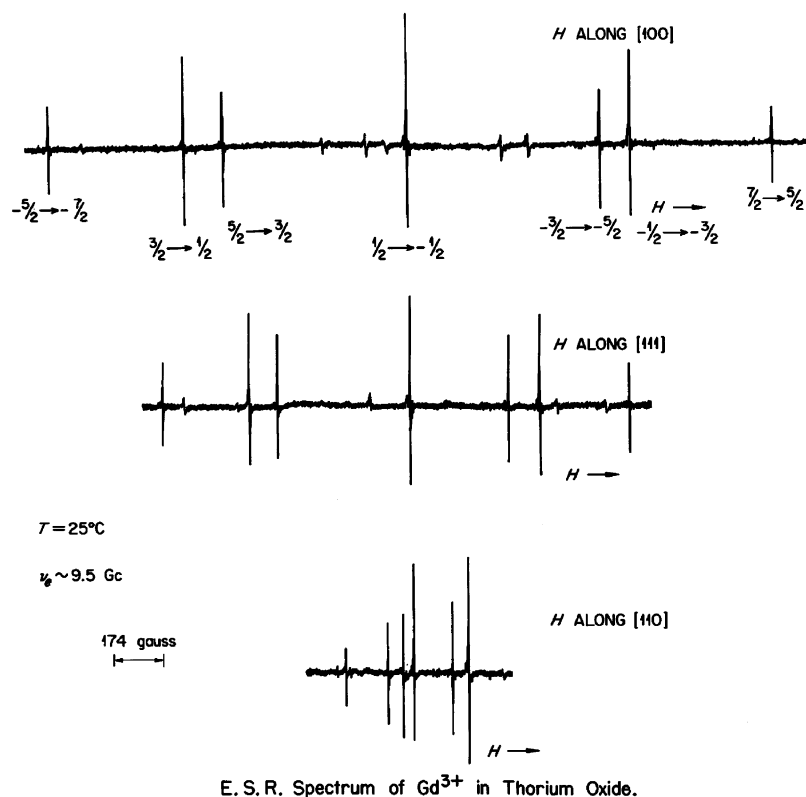


Fig. 2. EPR spectra of Gd^{3+} incorporated as a dilute impurity in a single crystal of ThO_2 . The spectra shown are in a first-derivative-of-absorption presentation with the applied dc magnetic field oriented along the [100], [110], and [111] crystallographic directions [92].

illustrates the energy-level structure resulting from the combined effects of a cubic crystal-field interaction and an applied magnetic field on the $^8\text{S}_{7/2}$ ground state of an ion like Gd^{3+} . As originally predicted by the symmetry considerations of Bethe [91] in 1929, a cubic field effect would split the eight-fold degeneracy into a Γ_7 doublet, a Γ_8 quartet and a Γ_6 doublet. The sign of the crystal-field interaction determines whether the lowest lying crystal-field level is the Γ_6 or the Γ_7 state. An applied dc magnetic field removes the remaining degeneracy yielding the eight energy levels shown in Fig. 1 [92]. In a standard EPR experiment, the sample is placed in a microwave field with the rf magnetic field component oriented perpendicular to the dc applied field. With this magnetic-field configuration (and depending on the magnitude of the splitting between the Γ_6 and Γ_7 levels), the seven $\Delta M_s = \pm 1$ transitions indicated in Fig. 1 can be observed. The “theoretical” EPR “stick” spectrum for an $^8\text{S}_{7/2}$ ion with the applied dc magnetic field oriented parallel to a [100] cubic crystal axis is illustrated at the bottom of Fig. 1 with the intensities of the transitions calculated using the Fermi Golden Rule. An actual EPR spectrum observed for Gd^{3+} incorporated as a dilute impurity in a single crystal of ThO_2 with H applied along a [100] crystal axis is illustrated at the top of Fig. 2 [92]. In this figure, the line shapes of the transitions represent the first derivative of the actual

absorption line due to the use of phase-sensitive detection in the extraction of EPR signals from the noise. The interaction with the applied dc magnetic field is anisotropic, and the EPR spectra illustrated at the middle and bottom of Fig. 2 are those obtained with the applied dc magnetic field oriented along the [111] and [110] cubic crystal axes, respectively. One of the more pleasant and intriguing aspects of EPR spectroscopy is tracing out the anisotropic angular variation of the EPR lines of $^8\text{S}_{7/2}$ (and other anisotropic spectra), and the angular variation of the spectrum of Gd^{3+} incorporated in a CeO_2 single crystal is shown in Fig. 3 [92]. Ultimately, I made many trips back-and-forth between Vanderbilt and ORNL learning the finer points of EPR spectroscopy from Marvin Abraham, and eventually I completed my thesis graduating with the Ph.D. degree in the Spring of 1966.

Following the receipt of my degree, I took a position in the research center of a now-defunct aerospace conglomerate. This job afforded me the opportunity to start my own research effort, to design and build my own EPR spectrometer, and to set up my own laboratory—and at the time, it seemed like a good idea. During the course of my thesis work on rare-earth ions, I had become intrigued with the problem of the Jahn–Teller (J–T) effect—an effect associated with the instability of degenerate energy levels and the tendency

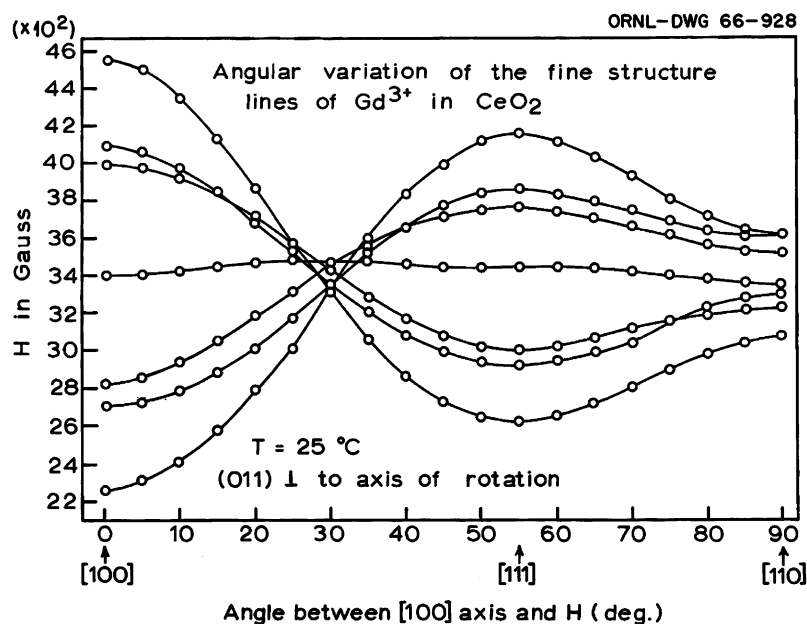


Fig. 3. Angular variation of the EPR spectrum of Gd^{3+} in a single crystal of CeO_2 [92]. This variation is observed when the applied magnetic field is rotated in the (110) plane of the CeO_2 cubic host crystal.

of systems to distort in a manner that results in the removal of this degeneracy. These were (and are) tough problems, and as a young researcher I felt that it was important for me to work on “hard” problems. I have found that this is a typical characteristic of young scientists who often lack the perspective and experience to appreciate how difficult it is to really understand the “easy” problems—much less the tough ones. This is, in actuality, a fortunate situation, because, otherwise without the young researchers, the tough problems might never be addressed at all. During two summers of working in the Central Research and Engineering Division of Texas Instruments (T.I.) in order to earn extra funds while in graduate school, I had met T.L. Estle—an outstanding scientist who had gone on to become a professor in the Physics Department at Rice University. During the course of interactions with Tom Estle while he was still at T.I., we discussed our mutual interest in applying EPR to the study of J–T effects, and in particular, to orbital doublet systems.

Once I completed my degree and began to set up my own laboratory in the aerospace-conglomerate research laboratory, Tom Estle and I met several times in order to outline a collaborative J–T project that would also involve a graduate student from the Physics Department at Rice. In the division of labor that we outlined, one of my responsibilities lay in the growth of the appropriately doped single-crystal samples (and their subsequent treatment in order to produce the required valence states) that we were to ultimately study. So, during the time that my EPR spectrometer was being designed and constructed, I worked on the crystal growth aspect of

our joint J–T project. After 6 months or so of crystal growth and reducing treatments, I prepared a fairly large set of “possible” samples and then took these specimens to Rice where they had a simple, but working, EPR spectrometer with cryogenic capability that was housed in the Physics Department. Working with a Rice Postdoc (Bernard Dischler) from Germany and J.R. (Jim) Herrington, a graduate student who was looking for a thesis topic, we began to examine the crystals. After a number of failed attempts to see any EPR spectra with the tell-tale J–T features, and with a limited supply of liquid helium, we finally resorted to loading four crystals at a time into the X-band microwave cavity. After several tries using this “shotgun” approach, and shortly before our entire stock of samples was going to be completely exhausted, we observed an EPR spectrum that exhibited the unusual characteristics of a J–T ion. Fig. 4 shows the energy level diagram for systems of this type and lists the different interactions that are involved in producing the unusual EPR spectra observed for J–T ions like La^{2+} where the crystal-field splitting produces an orbital doublet ground state [93–97]. Fig. 5 illustrates the angular variation of the EPR lines and the characteristic low-temperature spectral features for the case of a d^1 configuration ion (Sc^{2+} instead of La^{2+} in this example [95]) in an eight-fold-coordinated site in a single crystal of BaF_2 .

With four samples simultaneously in the microwave cavity in the initial experiments at Rice, we were not sure what crystal was actually giving us the signal; so we had to remove all of the crystals and then start examining them one-by-one. On the third try, we identified the

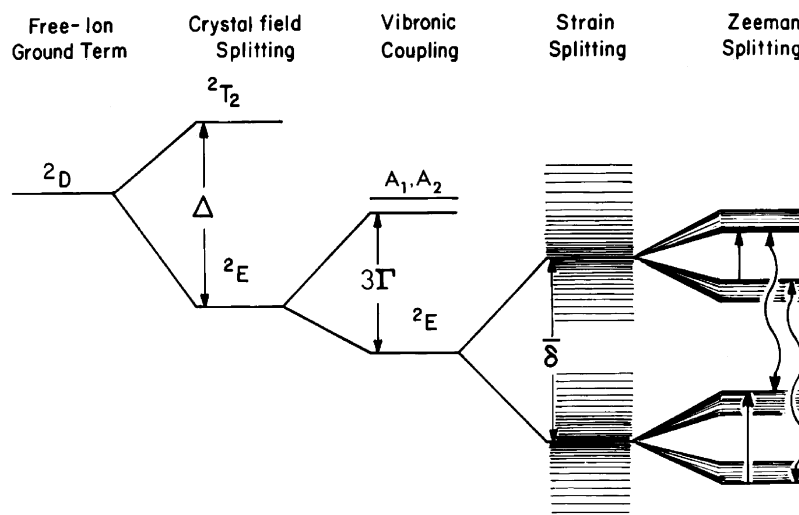


Fig. 4. Energy-level diagram for La^{2+} , Sc^{2+} , or Y^{2+} in an eight-fold-coordinated cubic site. The various interactions that split the free-ion ground state are indicated [94].

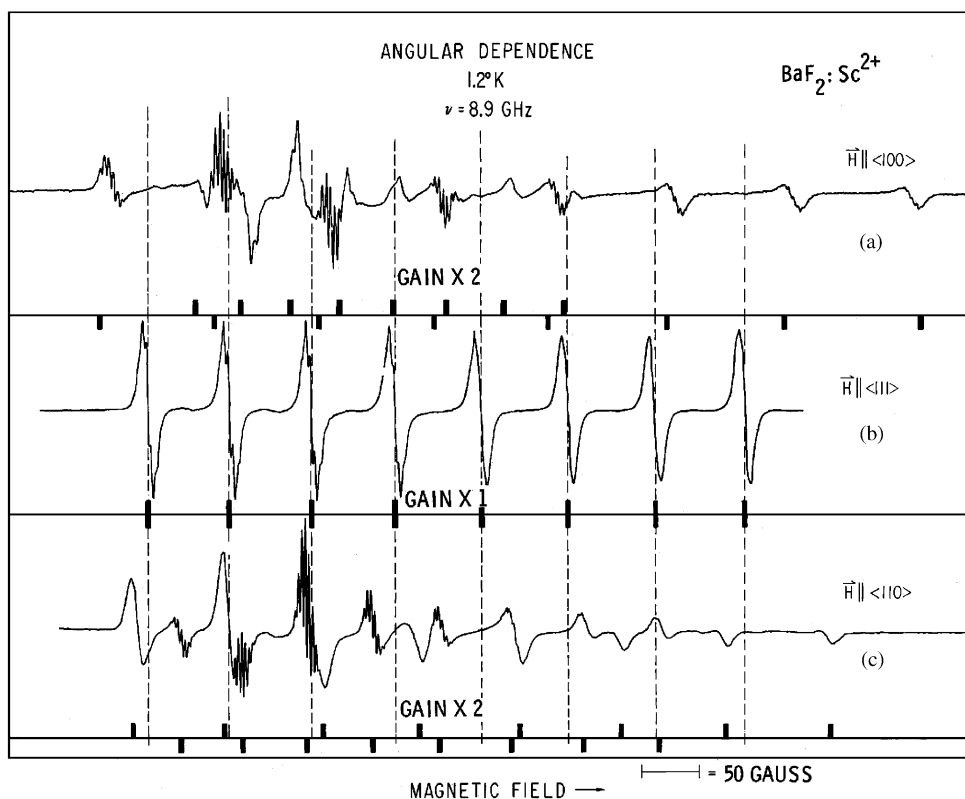


Fig. 5. EPR spectra showing the characteristics features of a J–T ion— Sc^{2+} incorporated as a dilute impurity in a single crystal of BaF_2 [95].

sample that had produced the EPR spectrum. It was a crystal of strontium chloride—a cubic fluorite-structure host that was doped with lanthanum.

In order to obtain an orbital doublet ground state using this host and a paramagnetic lanthanum impurity, it was necessary as noted above, to have a d^1 -configuration ion, namely La^{2+} , located in the eight-fold-coordinated cation substitutional site of SrCl_2 . This

necessitated a treatment to reduce the initially (normally) trivalent La ion to the divalent state. Among several potential approaches to carrying out the required valence change of La, I had decided to try a metal–vapor reduction process in which the doped SrCl_2 crystal is heated in a Sr metal vapor in a sealed ampoule. This was the process that had produced the La^{2+} -doped SrCl_2 sample that we had used with success in the first

experiments at Rice. The thing that I did not appreciate at that point was how critical the conditions for carrying out the metal–vapor–reduction process actually were. The interplay between the annealing temperature and time has to be just right. If the temperature is too high or the sample is annealed too long, then metallic colloids of Sr form in the crystal. It becomes brittle, crumbles, and the sample is no good. If the temperature is too low or the annealing time is too short, the reduction of La^{3+} to La^{2+} does not take place—and again, the sample is no good. Following our original success using the EPR spectrometer at Rice, it took over 6 months of hard work to learn how to reproduce the exact sample treatment that was required to form La^{2+} as a substitutional impurity in a single crystal of SrCl_2 and to get back to the point where the initial EPR results could be consistently reproduced. The fact that one of the original samples in the set had been subjected to the proper reducing conditions was a stroke of pure luck and good fortune. Once this critical sample preparation hurdle was overcome, however, things began to move expeditiously, and soon we had results that led to the publication of a Phys. Rev. Lett. [93] and a subsequent Phys. Rev. article [94] on EPR studies of the J–T effect for divalent lanthanum.

This initial work was followed by several years of collaborating with Tom Estle and Jim Herrington on a variety of studies of the J–T effect for d^1 -configuration ions such as Y^{2+} and Sc^{2+} in various fluorite-structure hosts in which the divalent ion was in an eight-fold coordinated site [93–97]. Jim Herrington wrote his Ph.D. dissertation based on this series of experiments, assumed a postdoctoral position in Germany, and eventually formed his own company in Texas making searchlights for boats. In later J–T work, Robert W. Reynolds and I built on the La, Y, and Sc experiments, and we observed intermediate J–T effects in systems where the orbital doublet ground state arose from d^p configuration ions like Ag^{2+} and Cu^{2+} in six-fold-coordinated hosts like MgO and CaO [98–101]. So, this later work on intermediate J–T effects did not involve a lanthanide or rare-earth-like ion (although it clearly built on work that did).

During the time of the work on EPR studies of J–T effects, the collaboration with Marv. Abraham on rare-earth and actinide ions continued and this collaboration eventually extended to the J–T work on Ag^{2+} and Cu^{2+} . The alkaline-earth-oxide host crystals doped with Ag^{2+} and Cu^{2+} were, in fact, grown by Abraham and colleagues at ORNL, and without these unique samples, the intermediate J–T experiments would not have been possible.

One important lesson was learned early on through interactions with excellent crystal growers like Cabell Finch and also through the ORNL capability and experience in the submerged-arc-fusion growth of the

alkaline-earth oxides. This lesson relates to the importance of obtaining high-quality research samples, and in particular, of being the first to obtain such specimens. If someone else has access to high-quality samples first, then they do the experiments first, and everyone else is left at the “end of the parade.” Another valuable lesson that I learned from my association with researchers at Oak Ridge was how one can sometimes use materials science to help in finding the solution to (or at least simplifying) physics or solid-state chemistry problems. A simple, straightforward example of what is meant by this is provided by Fig. 6. The top trace in this figure shows the EPR spectrum for a single crystal of SrCl_2 that contains a naturally abundant impurity of the S-state rare-earth ion Eu^{2+} . As shown in the figure, the spectrum consists of broad, not-well-resolved features due to overlapping hyperfine lines of the two Eu isotopes, ^{151}Eu and ^{153}Eu . This lack of resolution of the hyperfine structure effectively precludes accurate determinations of the hyperfine parameters of the Eu isotopes. By taking advantage of the availability of highly enriched stable isotopes, it is possible to grow single crystals of SrCl_2 that contain primarily only ^{151}Eu or ^{153}Eu and the sharp-line, well-resolved EPR spectra illustrated in parts *b* and *c* of Fig. 6 are obtained. With this kind of resolution, accurate measurements of the Eu

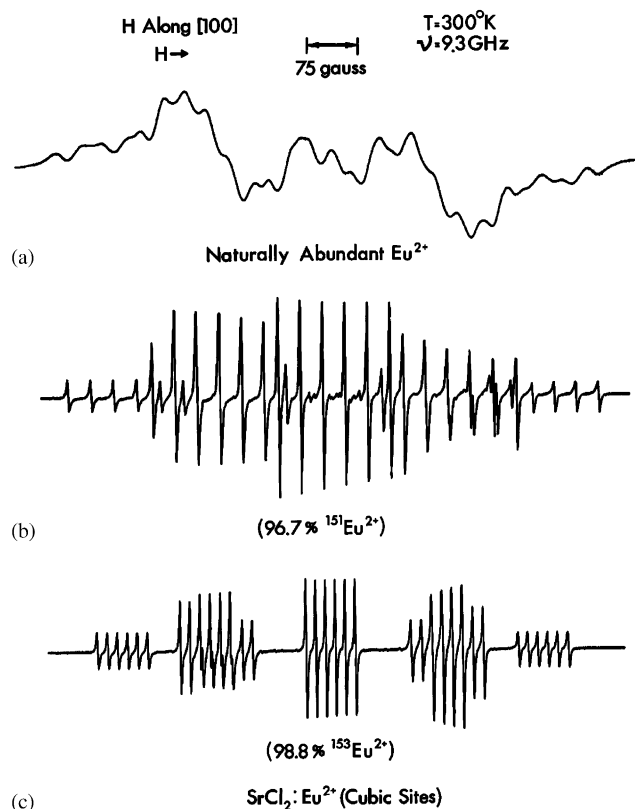


Fig. 6. EPR spectra of an Eu^{2+} impurity in a single crystal of SrCl_2 illustrating the utility of employing highly enriched isotopes in simplifying spectroscopic problems.

hyperfine parameters of the two isotopes can easily be made.

Through the association with the researchers at Oak Ridge, I had the rare and special opportunity of being a part of numerous EPR studies of actinide ions. These special and rare research materials were made by bombarding targets in the high-flux isotope reactor at ORNL, and the resulting isotopes were separated and purified in the hot cells of the ORNL TRU facility. The single crystals that contained the desired actinide isotopes were subsequently grown in glove box facilities in the ORNL Transuranic Research Laboratory. The actinide EPR studies encompassed the initial determination of the nuclear spins of some of the actinide isotopes and the first (and in a few cases, to this day, the only) observation of these isotopes by means of EPR spectroscopy. Fig. 7 shows an example of an actinide-ion EPR spectrum [82] that includes the isotopes ^{243}Cm , ^{244}Cm , and ^{241}Am incorporated as impurities in a single crystal of SrCl_2 . In the pursuit of actinide EPR studies, we made it all the way out to element 99, einsteinium [70], before research of this nature on the actinide elements was euphemistically “de-emphasized.” An EPR spectrum of $^{253}\text{Es}^{2+}$ as a dilute impurity in a single crystal of SrCl_2 is shown in Fig. 8 with the eight hyperfine lines in the spectrum arising from the $I = 7/2$ nuclear spin of ^{253}Es .

In 1977, Marvin Abraham and I wrote a review article on EPR studies of actinide ions [68] in which we summarized the results of investigations of this type to that point in time. In doing background reading for this review article, one of the things that made a lasting impression on me was the description of how difficult it was to chemically break down the mineral monazite in order to extract thorium or uranium. Really extreme chemical conditions are required for the decomposition of monazite—a mixed lanthanide orthophosphate REPO_4 (where RE represents the light rare earths).

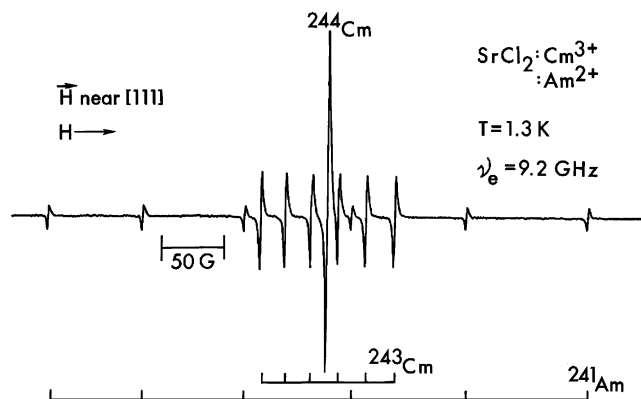


Fig. 7. The EPR spectra of three actinide isotopes incorporated as a dilute impurity in a single crystal of SrCl_2 . EPR spectra were used to carry out the initial determination of the nuclear spins of some actinide isotopes from observations of the hyperfine structure [82].

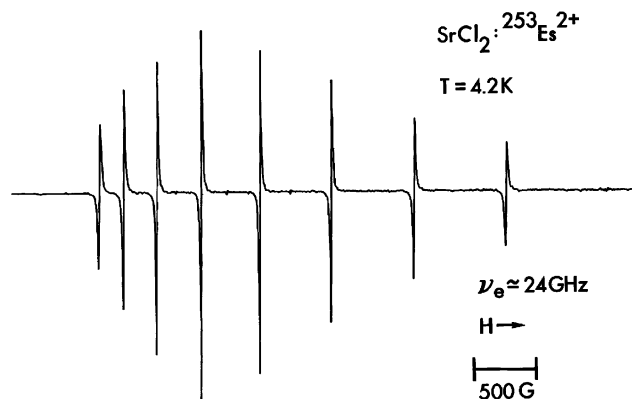


Fig. 8. The EPR spectrum of $^{253}\text{Es}^{2+}$ in a host SrCl_2 single crystal. Eight hyperfine lines are observed due to the hyperfine interaction with the $I = 7/2$ nuclear spin of ^{253}Es [70].

I had joined the ORNL Solid State Division in 1977, and not long after that, I was asked to outline a potential research project that could contribute to the field of materials for nuclear waste disposal. The impression of the chemical durability of the rare-earth orthophosphates was still fresh in my mind as a result of the reading that was done in preparing the actinide EPR review. Accordingly, it was only a small mental step to propose a classic approach of reverse engineering [102]—namely, to synthesize rare-earth orthophosphate matrices that, instead of only incorporating Th and U (like natural monazites), also incorporated other actinide (and non-actinide) radioactive waste ions. As luck would have it, the program officer at DOE who was in charge of this area of materials research at that time had, early on in his career, carried out X-ray studies of monazite. He knew about monazite; he liked the monazite waste-form idea, and it was funded immediately.

This new research support initiated a wide range of investigations of the properties of the rare-earth orthophosphates—some of which continue to the present time [103–134]—although not in the realm of materials for nuclear waste disposal. In addition to fundamental studies of the properties of the rare-earth orthophosphates, a significant effort has gone into the development of applications of these materials. These applications include the development of a set of orthophosphate microprobe standards for rare-earth analysis that is in use worldwide [135], the discovery of new materials for use as gamma and X-ray detectors [136], and the use of lanthanide orthophosphates as hosts for micro-lasers [130]. So, it is possible to start out using EPR spectroscopy to study the fundamental properties of rare-earth and actinide ions or the intricacies of the J–T effect and wind up working on the development of materials for nuclear waste disposal.

Acknowledgments

I would like to take the special occasion of receiving the Frank H. Spedding award to sincerely acknowledge individuals whose contributions, decisions, and help have been critical in my professional life. Among others, these are: Henry C. Thomas, Dean Severence, Tom Pinkston, Marvin M. Abraham, Thomas Estle, Robert W. Reynolds, B. R. Appleton, Rodney Ewing, Michel Rappaz, and André Châtelain.

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