

Rice University
Physics 332

ELECTRON SPIN RESONANCE

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I. Introduction

Optical spectroscopy has been enormously useful for exploring the energy levels and excitations of atomic systems at electron-volt energies. For understanding solids, however, one would like information at milli-eV energies, so different forms of spectroscopy become important. In this experiment we will study one spectroscopic method known variously as electron paramagnetic resonance, EPR, or electron spin resonance, ESR. The technique depends on the fact that certain atomic systems have a permanent magnetic moment. The energy levels of the magnetic system are influenced by the surrounding atoms and by external magnetic fields. Transitions among the levels can be detected by monitoring the power absorbed from an alternating magnetic field, just as ordinary atomic transitions are detected by absorption of light. Comparing the observed transitions with model calculations then lets us deduce some features of the environment around the moment.

The experiment has several parts. First, we need to set up the conditions to detect the EPR and test the effect of various spectrometer parameters. The signals are quite weak so this also serves to demonstrate the lock-in amplifier as a signal recovery device. Once we can use the equipment effectively we can compare the spectra of Cr^{+3} in two different hosts to see what EPR can tell us about the atomic environment of a known ion. The last exercise will be the study of a crystal containing unknown impurities to show how EPR could be used as an analytical tool.

The discussion below only scratches the surface of EPR applications. Some of the better texts available for further study are:

The Physical Principles of EPR, by Pake and Estle. An excellent elementary introduction.

EPR of Transition Ions, by Abragam and Bleaney. The definitive (911 pp) compendium.

Principles of Nuclear Magnetism, by Abragam. Strictly concerned with NMR but much of the physics is the same and the explanations are elegant.

EPR: Techniques and Applications, by Alger. The grubby details.

II. Theoretical Considerations

To understand the phenomenon of EPR one needs to consider three main issues: What atomic systems can exhibit permanent paramagnetism? What are the energy levels of a particular paramagnetic system in the presence of an external magnetic field? and How do we detect transitions among the levels? These are obviously interrelated but for convenience we consider each in turn.

A. Paramagnetic entities

Magnetism arises from the motion of charge on an atomic or sub-atomic (nuclear) scale. Since charge is inevitably associated with mass, this implies an intimate relation between the angular momentum and the resultant magnetic moment of an atomic entity. The simplest case occurs for spherical symmetry (an isolated atom) when the orbital and spin angular momenta are good quantum numbers. Then the magnetic moment of the atom is given by the ground-state expectation value of the magnetic moment operator

$$\vec{\mu} = -\mu_B(\vec{L} + g_e\vec{S}) \quad (1)$$

where μ_B is the Bohr magneton and $g_e \approx 2$ is called the electronic g-factor. (Several useful numbers, including these, are tabulated in the Appendix.) A similar expression can be written for a nucleus with net angular momentum.

Equation 1 implies that isolated atoms or ions will frequently have magnetic moments since outer-shell electrons will be not all be paired, except in the rare-gas configurations. Most bulk matter, however, does not exhibit paramagnetism. The magnetism is suppressed because chemical bonding requires transfer (ionic bonds) or sharing (covalent bonds) of electrons in such a way that both atoms acquire a rare-gas configuration. Nuclei, of course, do not form chemical bonds and hence nuclear magnetism is quite common in solids.

There are a number of ways for condensed matter to retain some magnetic moments, the most important of which involve certain unusual molecules, transition-group atoms, or particular point defects in solids. Molecular NO and NO₂ both have an odd number of electrons and hence a permanent magnetic moment. Similarly, many large molecules can exist with an odd number of electrons. Completing this group, the ground state of O₂ happens to be a partially-filled shell with corresponding moment. Transition-group atoms are those which have incomplete 3d, 4d, 5d, 4f or 5f shells. Bonding of these atoms often involves higher-energy p or s electrons, leaving the unpaired d or f electrons relatively undisturbed. When this occurs the atom or ion retains

nearly the full atomic moment. Finally, certain defects such as vacancies or foreign atoms in a crystal may gain or lose an electron relative to the chemically bonded host, thereby producing a localized moment.

Here we will be concerned with only two types of magnetic entity. The simplest magnetically is a large organic molecule known as DPPH ($\alpha\alpha'$ -diphenyl- β -picrylhydrazyl). It has a single unpaired electron, leading to a very simple energy level structure. We will also study some of the typical 3d transition elements when present at low concentration in insulating crystals. By considering only dilute solid solutions of the 3d atoms we avoid atom-atom interactions which complicate the interpretation of EPR spectra. (In other circumstances the interactions are of considerable importance, leading for example to the magnetism of metallic iron.)

B. Energy levels

The energy levels of a magnetic moment with no orbital angular momentum ($L = 0$) are quite simple. In the presence of a magnetic field the degenerate ground state splits according to the Zeeman Hamiltonian

$$H_z = -\vec{\mu} \cdot \vec{H} \quad (2)$$

into $2S + 1$ levels characterized by S_z . At any given field the separation between adjacent levels is constant at $g\mu_B H$. For g -values near g_e and typical laboratory fields of 10 kG this splitting is rather small, about 10^{-4} eV.

Although not free, the unpaired electron in DPPH behaves approximately like this with $S = 1/2$. Similarly, some atoms with half-filled shells may have $L = 0$. The Mn^{2+} ion, which has a $3d^5$ configuration with $L = 0$, $S = 5/2$ is a good example. In an external field the 6S ground state of Mn^{2+} splits uniformly as a free spin would.

When an atom is incorporated into a crystal the situation becomes a good deal more interesting, particularly if $L \neq 0$. Generally the atom will lose one or more electrons to become a charged ion similar (but not necessarily identical) to the host atoms. The ion is also subject to interactions with the surrounding electrons and nuclei which will perturb its energy levels. Obviously, calculation of the resulting energy levels in the general case would be a formidable problem in quantum mechanics even if one knew all the pertinent parameters.

To keep matters reasonably simple, we will explicitly consider only a 3d atom for which the Russel-Saunders coupling scheme is adequate. The Hamiltonian for the ion is then the sum of several terms:

$$H = H_0 + \lambda \vec{L} \cdot \vec{S} + A \vec{I} \cdot \vec{S} + H_{cf} + H_z \quad (3)$$

The first term is the usual free-atom Hamiltonian, except for two parts which are written explicitly. The spin-orbit coupling is the second term, while the $A\vec{I}\cdot\vec{S}$ term describes the "hyperfine" coupling of the electronic spin to the nuclear spin \vec{I} . We use H_{cf} to represent the electrical interaction of the paramagnetic species with the neighboring atoms, including effects due to bonding. In the simplest approximation the interaction can be thought of as due to point charges at the surrounding host sites, hence the common name "crystal field". By relating H_{cf} to the observed EPR spectrum we hope to learn something about the surroundings of the ion. The last term is the Zeeman interaction, given by Eq. 2. In principle we should include the nuclear Zeeman Hamiltonian also, but it is too weak to be of concern here.

Ignoring the Zeeman and hyperfine terms for the moment, we need to solve for the eigenvalues and eigenvectors (wavefunctions) of Eq. 3. At first sight we might try to treat the spin-orbit and crystal field as perturbations, but this is inadequate. For 3d ions the spin-orbit interaction is weak, but the crystal field strength can be comparable to the electron-electron interaction contained in H_0 . We must usually, therefore, include H_{cf} from the beginning and then treat the spin-orbit, hyperfine and Zeeman terms as perturbations. The calculations are difficult but can be done when the surroundings are reasonably symmetric. For example, Fig. 1 shows a typical energy level diagram for Cr^{3+} when H_{cf} has octahedral symmetry. (Imagine the ion site at the origin and then put equal charges at equal distances along the $\pm x$, $\pm y$ and $\pm z$ directions. The electrostatic field produced by those charges has octahedral symmetry.) The Hund's-rule ground

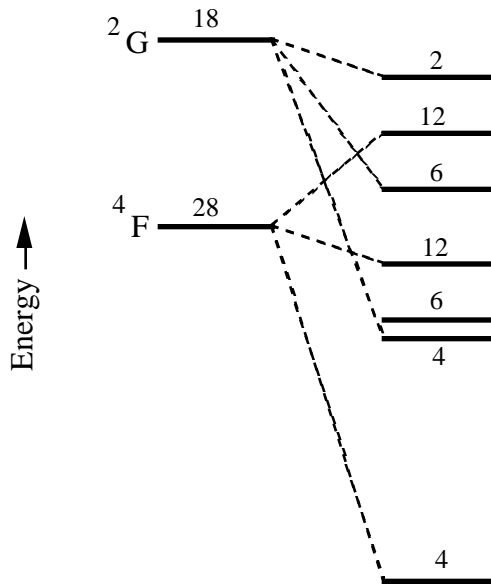


Fig. 1 Energy levels of Cr^{3+} in an octahedral crystal field, compared to the free-ion levels. The degeneracy is noted for each level. The overall crystal field splitting is about 3.5 eV in typical hosts.

state for the free $3d^3$ ion has $L = 3$, $S = 3/2$, while the first excited state has $L = 4$, $S = 1/2$. The crystal field has partially lifted the degeneracy of the spherically symmetric ion to form a complicated array of levels. The wavefunctions of these levels are generally mixtures of several of the free-ion wavefunctions. As you can infer from the caption, transitions among these levels will be driven by optical frequencies and can account for the visible colors of crystals containing Cr^{3+} .

At any reasonable temperature only the lowest level in Fig. 1 is populated. Accordingly, we need only consider the effect of an applied field on the lowest state. If $A = 0$ (no nuclear moment) the perturbation calculation requires evaluation of various matrix elements of H_z with the wavefunctions for the ground state. One finds that the field lifts the four-fold degeneracy, splitting the state into the four equally spaced levels diagrammed in Fig. 2a. It is amusing to note that a free moment with $L = 0$, $S = 3/2$ would split in the same way, although the g-value may differ in the present situation. We have used this fact to label the states with a fictitious spin quantum number \tilde{M}_s , and will pursue the point later.

When the hyperfine interaction is present we must solve a slightly more complicated problem, since the electronic energy will depend on the orientation of the nucleus as well as the applied field. The result is shown in Fig 2b for $I = 3/2$. The distinctive feature here is that, at high field, each electronic level is split into $2I + 1$ levels, corresponding to the $2I + 1$ possible values of I_z . For convenience, we have again labeled the states with the fictitious quantum number \tilde{M}_s , as well as I_z . Very crudely, one can think of the z-component of the magnetic field due to the

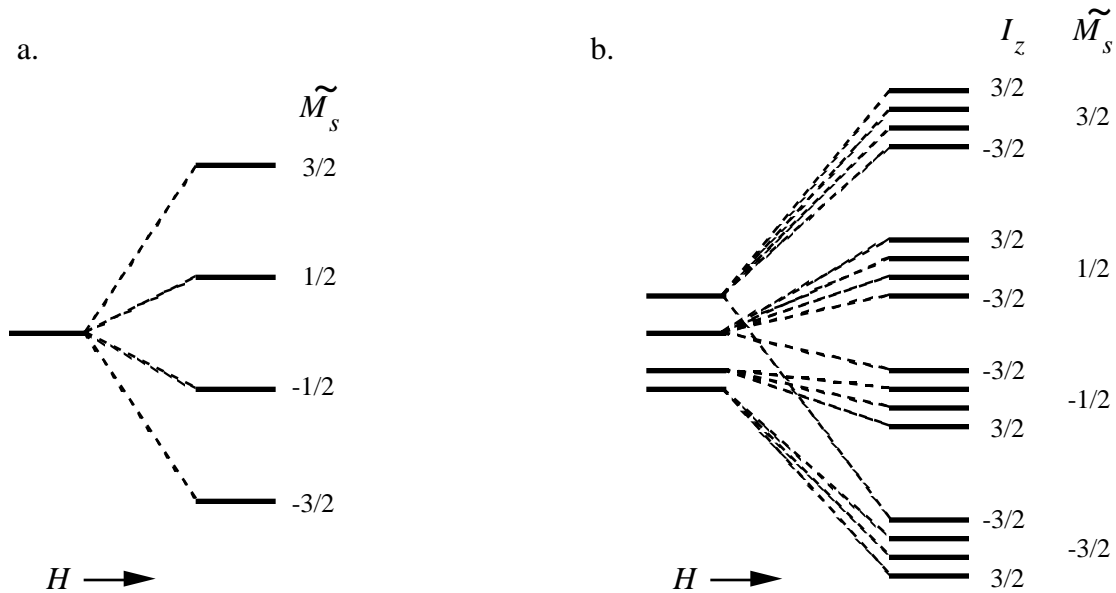


Fig. 2 Splitting of the ground-state energy levels of Cr^{3+} in a magnetic field for: a. Spinless nucleus, $A = 0$; b. Nucleus with spin $I = 3/2$.

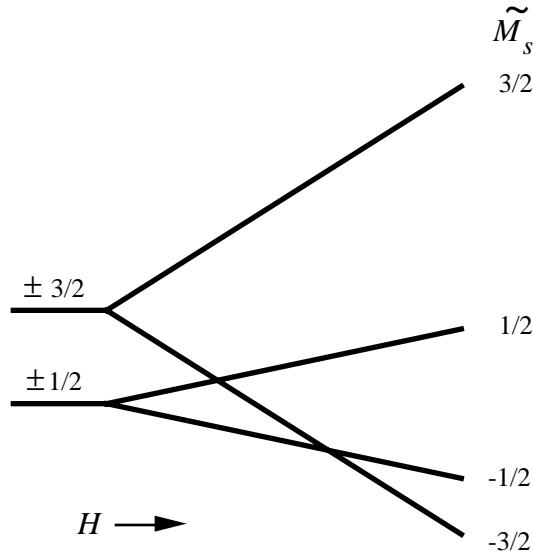


Fig. 3 Splitting of the ground-state energy levels of Cr^{3+} in a host with distorted octahedral symmetry. The field-induced splitting assumes H along the distortion axis. The energy levels will shift if H is applied in other directions.

nucleus either aiding or opposing the external field.

So far we have assumed a particular, highly symmetric crystal field. Consider now putting the same ion into a different host, in which the octahedral symmetry is disturbed by stretching the charge distribution of the host along some particular axis. (The case we use is a trigonal distortion, corresponding to stretching along the line $x=y=z$.) The result is shown for Cr^{3+} in Fig. 3, with the customary fictitious spin labels. Including a non-zero hyperfine interaction would simply split the levels as before, so we have omitted it. Two new features are present here. Evidently the four-fold degeneracy is partially lifted even in the absence of the field. Not shown is the fact that the field-dependent splitting will now vary with the angle between the field and the distortion axis. In effect the distortion has picked out a direction in the crystal and the energy levels can depend on the angle between that axis and the external field.

C. Detection of transitions

Once we have found the energy levels it is reasonable to ask how we can detect them. Our experience with atomic systems suggests looking for absorption of electromagnetic radiation due to transitions between levels. We expect that this absorption will occur when $h\nu = \Delta E$. Since we are dealing with magnetic phenomena, we would particularly expect to see energy absorption in response to the alternating magnetic field of the radiation.

We can formalize this idea by considering a time-dependent Zeeman Hamiltonian

$$H'_z = -\vec{\mu} \cdot \vec{H}' \cos 2\pi\nu t \quad (4)$$

assuming a linearly polarized field. The magnitude of \vec{H}' is usually small, so we can treat this as an additional time-dependent perturbation inducing transitions between the energy levels previously calculated. Carrying out the calculation one finds that the rate of transitions between an occupied state M and an unoccupied state M' is proportional to the matrix element $\langle M' | H'_z | M \rangle^2$ whenever $h\nu$ is equal to the difference in energy between the states. Since M' will normally be higher in energy than M a transition from M to M' implies an absorption of energy from the source of the time-varying field. If the paramagnetic system can subsequently lose the energy, for example as heat, the process can continue indefinitely.

One other feature emerges from the calculation. The matrix element $\langle M' | H'_z | M \rangle^2$ is non-zero only for certain pairs of states M, M' . For a simple free spin the selection rule is quite strong: all non-zero matrix elements have $M'_s = M_s \pm 1$. Since the level splittings are all equal, this means that all transitions occur at the same frequency. The ΔM_s rule also applies when a hyperfine interaction is present to give a level structure as in Fig. 2b. The nuclei are unaffected by the time varying field, which is far from their resonant frequency, so $\Delta I_z = 0$, leaving $2I + 1$ possible distinct transitions. Departing from the free-spin case, one finds that the selection rules depend on the details of the ion and the symmetries of the environment. Except when the symmetry is rather high, the matrix elements must then be evaluated individually.

The experimental requirements should now be reasonably clear. The specimen containing the paramagnetic atoms is placed in a uniform magnetic field and a small alternating magnetic field is applied. We then arrange to detect the absorption of energy when the frequency of the alternating field is equal to one of the transition frequencies of the system. Quantitatively, the needed frequencies are usually in the microwave region, 1-10 GHz for applied fields of a few kilogauss. Since microwave apparatus operates over rather narrow frequency bands it is in fact more practical to sweep the main field and hold the frequency fixed than it is to vary the frequency. Fortunately this makes little difference in principle. The resulting EPR spectrum of energy absorption vs field is shown schematically in Fig. 4 for one of the energy level diagrams previously discussed.

D. Spin Hamiltonians

A complete calculation of the ionic energy levels in the presence of the crystal field, as used above, is not always available. This is particularly true when investigating a new ion-host combination. Such situations can be handled by extending the fictitious spin idea introduced above and creating a "spin Hamiltonian" to describe the observed splittings of the ion. The purpose of this construction is to supply a concise summary of experimental EPR results which

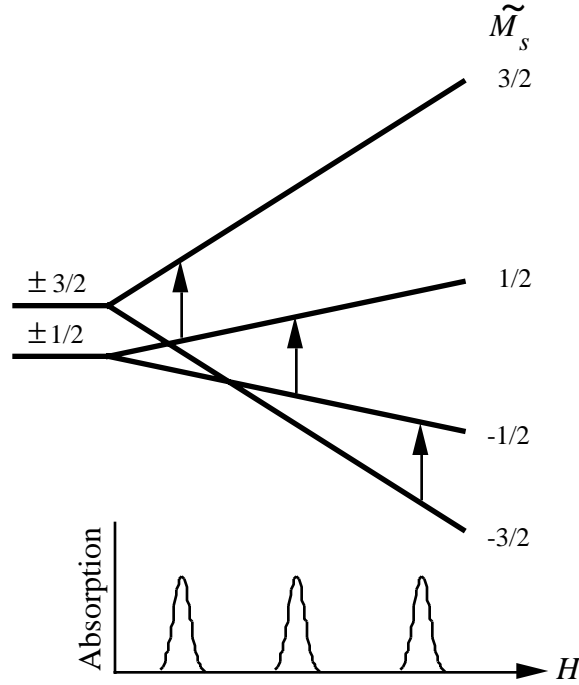


Fig. 4 The same levels as in Fig. 3, showing the three EPR transitions allowed by free-spin selection rules. The lower figure is a sketch of the expected EPR absorption spectrum as a function of field.

can later be compared with other data and with a proper quantum mechanical calculation.

In constructing the spin Hamiltonian we pick a value of S consistent with the known or suspected degeneracy of the ground state. The required value of S is, of course, not necessarily the same as that of any free ion state since interactions with the host will usually reduce the degeneracy of the ion. The Hamiltonian itself consists of all possible terms consistent with the symmetry of the surroundings and the magnitude of the spin. Any necessary parameters are left as unknowns. The result is usually fairly simple compared to a proper atomic Hamiltonian. The energy level calculation is carried through and the values of the unknown parameters are determined by comparison with the observed EPR spectra. If the calculated energy levels cannot fit the observations, the site or impurity must not have the assumed characteristics and another attempt is in order.

Some examples may clarify this process. The simple level diagram in Fig. 2a is described by the spin Hamiltonian

$$H = g\mu_B \tilde{S} \cdot \vec{H} \quad (5)$$

with the single unknown parameter g . The level is actually four-fold degenerate, requiring

$\tilde{S} = 3/2$, but $\tilde{S} = 1/2$ would describe the spectrum just as well since we see only one transition, which occurs when $h\nu = g\mu_B H$. In fact we use this relation as the experimental definition of g .

The presence of the hyperfine interaction, as in Fig. 2b, simply requires the addition of a hyperfine coupling term

$$H = g\mu_B \tilde{S} \cdot \vec{H} + A \vec{I} \cdot \tilde{S} \quad (6)$$

Again, either $\tilde{S} = 3/2$ or $\tilde{S} = 1/2$ would suffice. If the free-spin selection rules are obeyed, there will be transitions when $h\nu$ equals $g\mu_B H + (3/2)A$, $g\mu_B H + (1/2)A$, $g\mu_B H - (1/2)A$, and $g\mu_B H - (3/2)A$. Note that these will be spaced at intervals of $A/g\mu_B$ in applied field. In fact, if we did not already know the nuclear spin I we could determine it by counting the $2I + 1$ equally-spaced hyperfine components.

The level diagram in Fig. 3 requires a term which will be anisotropic in field and which will split the levels even when $H = 0$. A form with $\tilde{S} = 3/2$ and the necessary ingredients is

$$H = D\tilde{S}_z^2 + \mu_B \left[g_{\parallel} \tilde{S}_z H_z + g_{\perp} (\tilde{S}_x H_x + \tilde{S}_y H_y) \right] \quad (7)$$

The $D\tilde{S}_z^2$ term accounts for the zero-field splitting, while the apparent g -values will vary depending on the components of \vec{H} with respect to the distortion axis. (To be completely honest, we should also admit that both terms will contribute to the observed anisotropy when $g\mu_B H \leq D$, as occurs in our samples.) Because we see more than one transition, we definitely need $\tilde{S} = 3/2$ this time. Finally, note that with the addition of a hyperfine term all three cases could be written in the form of Eq. 7.

III. Methods and Measurements

A good deal of unfamiliar apparatus is needed to carry out this experiment. A microwave generator and resonant cavity provide a time-varying magnetic field. A lock-in amplifier is used to detect the minute reduction in microwave power produced by the EPR absorption. Finally, we use nuclear magnetic resonance, NMR, of protons to precisely calibrate the steady magnetic field. Because of this complexity you should first go through a careful set-up and check procedure using the strong and simple signal from a large sample of DPPH. Once convinced that the spectrometer is working, you can measure the EPR of Cr^{3+} in two different crystal environments. If time allows, you might then find it amusing to try a sample of "pure" MgO to see if you can discern what paramagnetic impurities it contains.

The next several sections describe how to tune each major item of equipment. Additional information will be found in the manufacturers' instruction manuals available in the lab. We conclude with the measurement of transition ions in insulating hosts.

A. Microwave system

The required alternating field H' is produced by a solid state oscillator operating near 8.9 GHz. The oscillator is coupled to a resonant cavity containing the sample. When the oscillator frequency matches the cavity frequency the amplitude of H' is increased relative to the oscillator amplitude by the Q-factor of the cavity. Since $Q \approx 3000$ this substantially enhances the field intensity and hence the absorption by the sample.

Some of the power entering the cavity is allowed to leak out the opposite side. The amount of leakage is determined by the input power and by sample absorption. The output power falls on a diode which converts it to a near-DC. This voltage, proportional to the transmission through the cavity, constitutes our signal. It is amplified for display on the instrument's meter and is also available at the front panel output jack.

Set up the MicroNow model 810B spectrometer as shown in Fig. 5. Gently place the DPPH sample tube into the cavity through the opening in the gold-colored collet. You are now ready to adjust the spectrometer.

1. Set the meter switch to read XTAL CURRENT, which is the current from the detector diode. (Diodes used to be called "crystals", abbreviated "xtal".) The reading is proportional to the power transmission through the cavity.

2. Use the TUNING VOLTAGE control to maximize the diode current reading. This changes the frequency of the microwave oscillator by changing its operating current until the frequency matches the resonant frequency of the cavity. The amplitude of H' and the transmission through

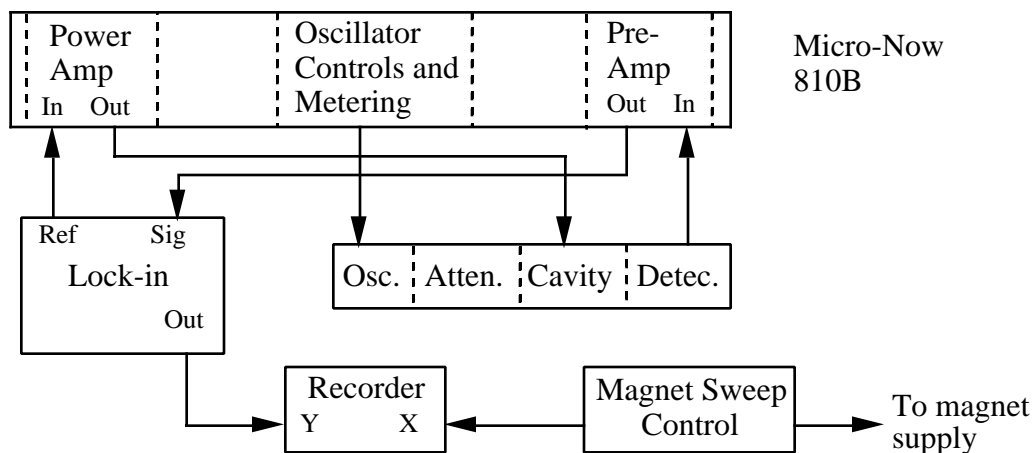


Fig. 5 Connection diagram for EPR apparatus.

the cavity are both maximum at the cavity resonance frequency.

3. There is a sliding metal plate behind the diode detector. The plate reflects the incoming microwaves to create a standing wave with an E-field maximum at the diode. Using the large knob on the detector mount, position the plate for maximum diode current. The adjustment is not critical and can be left undisturbed for the remainder of the experiment.

4. Measure the operating frequency with the wavemeter. This is an accurately calibrated adjustable resonant cavity weakly coupled to the output waveguide. At its resonant frequency it absorbs a fraction of the transmitted power, causing a dip in the diode current. Carefully tune the wavemeter near 8.9 GHz until you see the current dip sharply. By precisely setting the wavemeter for minimum current you can measure the oscillator frequency to four significant figures. When not measuring frequency, detune the wavemeter so it does not interfere with the EPR signals.

B. Magnet system

The main external field is produced by a large electromagnet. The power supply controller allows the field to be ramped slowly up or down, and also provides an output for a chart recorder. The controller has knobs to set the center point and width of the swept field range. Another control varies the sweep time from minimum to maximum field in several steps from about 15 s to 10 min. Two sets of push buttons are provided to start and stop the sweep and to set the field at the minimum, center or maximum of the specified range.

1. Turn on the cooling water at the sink. An interlock prevents operation of the magnet if the flow is too small. If the magnet coils get distinctly warm, increase the flow.

2. Turn on the sweep controller and the Hewlett-Packard power supply.

3. Set the controls for a range from 22.5 to 24 A, as read on the power supply meter. Use a 30 s sweep time. These settings should give a reasonable starting point for the DPPH signal.

C. Lock-in amplifier

As applied to EPR, the use of the lock-in is illustrated in Fig. 6. We apply a strong slowly-increasing field and a weak alternating field so that the instantaneous field seen by the spins is their algebraic sum. This causes the microwave power absorbed by the spins to vary at the frequency of the alternating field. The amplitude of the variation is proportional to the field derivative of the absorption at that total field strength. The varying power absorption is detected by a microwave diode which produces an AC signal at the frequency of the alternating field. The diode signal is used as the input to a lock-in amplifier.

Within the lock-in there is a tuned amplifier which preferentially amplifies signals at the modulation frequency. This is followed by a phase sensitive detector which multiplies the incoming signal by a reference square wave with the same frequency as the signal. The time-average value of the phase sensitive detector output is proportional to the amplitude of the input signal times the cosine of the relative phase between the reference and input voltages. An RC circuit with adjustable time constant is included to do the averaging before the output is sent to a recorder. Since the amplitude of the AC signal at the input is proportional to the derivative of the absorption, the XY recorder effectively plots that derivative vs field.

Adjustment of the lock-in is simple if you proceed systematically. Connect the lock-in to the

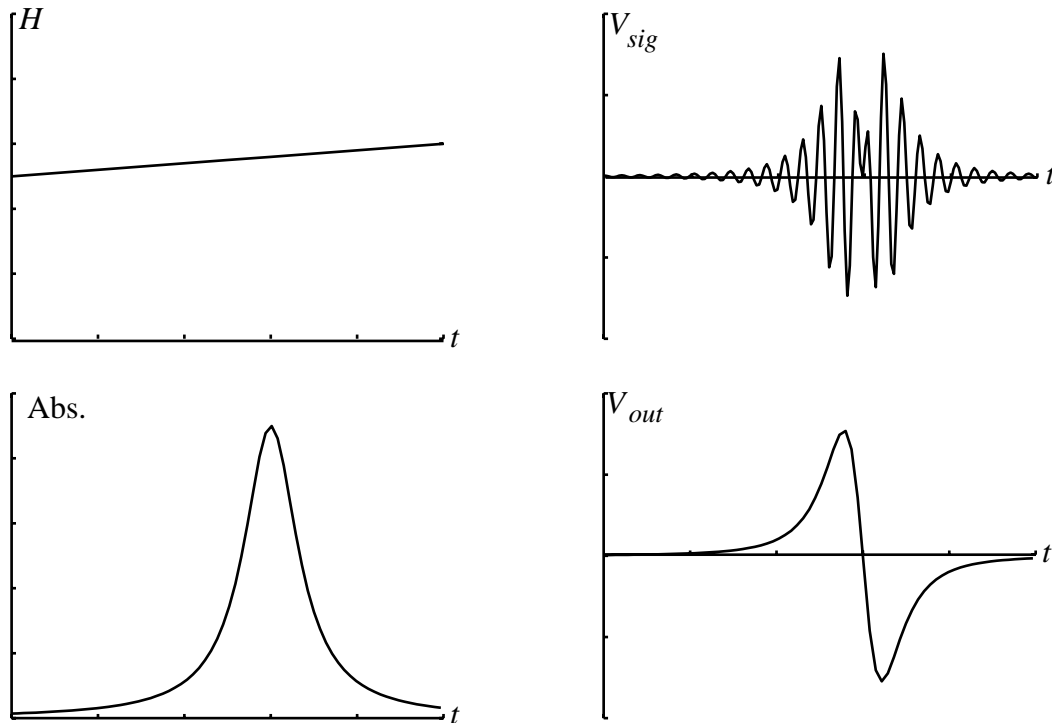


Fig. 6 Schematic plots of various quantities vs time: External magnetic field, averaged microwave power absorption, output of tuned amplifier and averaged output of PSD.

spectrometer electronics as in Fig. 5. An oscillator internal to the lock-in is used as input to a power amplifier which drives a coil inside the cavity. The field from this coil is parallel to the main field, as required. The same oscillator supplies the reference signal for the phase sensitive detector in the lock-in. The signal from the diode preamp is connected to the input of the lock-in and eventually becomes the signal input to the phase sensitive detector.

1. Connect the MONITOR output of the lock-in to one channel of the scope (AC coupled input) and the reference signal (with a tee) to the other channel. Trigger on the reference signal. Set the lock-in controls as follows:

SENSITIVITY: .5 mV

REFERENCE MODE: INT(ernal)

TIME CONSTANT: 0.1 s

2. Set the METER/MONITOR switch to SIG(nal). This connects the monitor output and meter to the tuned amplifier in the lock-in. Adjust the magnet current to either side of the DPPH peak absorption. The proper field is easily set by watching the scope and slowly sweeping the field to a point where there is a substantial MONITOR signal. The lock-in meter will also show a deflection which should be maximized to provide a strong signal for adjusting the phase.

3. Set the METER/MONITOR switch to OUT X1 and decrease the SENSITIVITY to get an on-scale reading. You are now looking at the averaged output of the phase sensitive detector. Adjust the PHASE controls to maximize the meter reading, thereby setting the relative phase between signal and reference voltages to zero. This procedure compensates for the various phase shifts between the modulation and the response of the spin system.

D. Initial measurements

At this point the spectrometer system should be properly set to observe the DPPH resonance. If other adjustments seem necessary, consult the instructor before proceeding. Otherwise, sweep the field through the DPPH resonance and plot the lock-in output on the chart recorder. You should obtain a clear derivative signal on the chart. Change the magnet sweep center and range so that the signal nicely fills the middle third of the x-axis.

Using the DPPH signal, explore the effect of the following changes and describe the results in your report. (Be sure to reset to standard conditions after each observation.)

1. Sweeping through the resonance with increasing or decreasing field.
2. Increasing the TIME CONSTANT to 1 and 3 s.
3. A small change in lock-in PHASE setting.
4. A small change in microwave frequency, obtained by adjusting the TUNING VOLTAGE for $\approx 10\%$ reduction in diode current when off the DPPH resonance.

It should be evident that for precise measurements of amplitude or resonant field we need to be

careful that all components are properly adjusted.

The next exercise is to precisely measure field and frequency for the DPPH resonance to determine the g -value. Although not of great interest, it provides a good check of the procedures to be used later. The microwave frequency measurement was described above. The microwave oscillator is usually stable but you should check the frequency again anyway. Do not forget to detune the frequency meter when finished. The magnetic field is measured with an NMR gaussmeter. Set it up following the instructions in the operator's manual available in the lab. If you have trouble finding the proton resonance, get help. It is a touchy instrument and you will see nothing until all the settings are rather close to optimum.

Having found the NMR signal, calibrate the recorder chart by noting the NMR frequencies at the minimum, center and maximum of the sweep range. Mark these points on the chart. The sweep control lets you set these fields quite reproducibly, a claim you should check. Now sweep through the DPPH resonance in both directions using a speed and TIME CONSTANT setting you have found satisfactory. Be sure to sweep a wide enough range to see the baseline but not so wide that the resonance location is ill-defined.

The analysis is essentially trivial. Maximum absorption corresponds to the zero-crossing of the derivative signal. Find the average position of the zero-crossing for the up and down sweeps and then interpolate between the calibration points to find the corresponding field. The g -value is defined by Eq. 5 with $\tilde{S} = 1/2$. Within your estimated errors, the result should agree with the accepted value of 2.0036.

E. Cr^{3+} in MgO

Magnesium oxide, MgO , is a fairly simple cubic crystal. The atoms occupy the vertices of an array of joined cubes, with Mg and O atoms alternating in all directions. Small amounts of Cr added to the growth medium can become incorporated into the lattice, giving the normally colorless crystal a greenish hue. (See Fig. 1 for the energy levels.) If Cr goes in substitutionally for Mg, as one might expect in an ionically bonded crystal, the surrounding O^{2-} ions will produce a crystal field of octahedral symmetry.

Evidently we could check this assumption by doing an EPR experiment, since we know that the form of the spectrum should follow from the energy-level diagram of Fig. 2a. Actually, there is a modest complication. Chromium has several isotopes: ^{50}Cr , $I=0$, 2.4% abundance; ^{52}Cr , $I=0$, 83.8%; ^{53}Cr , $I=3/2$, 9.6%; and ^{54}Cr , $I=0$, 2.4%. All the $I=0$ isotopes will contribute to a simple single-line spectrum. The ^{53}Cr atoms will produce a four-line spectrum according to Fig. 2b. If we can detect the four-line pattern, we can verify that we are actually observing Cr by checking the spin and abundance. The complication has become an advantage.

When starting measurements on a new sample it is probably most useful to survey the

territory and then work down to the features of interest. The following approach is typical.

1. Install the MgO:Cr^{3+} crystal. Adjust the microwave tuning voltage to maximize the diode current. This is necessary because the crystal, like any dielectric, shifts the cavity resonance frequency.

2. Set the lock-in SENSITIVITY to 1 mV and TIME CONSTANT to 0.1 s. This gives a fairly high gain which should make most signals visible without an excessively noisy baseline.

3. Set the magnet controls to sweep all or most of the available field range ($0 \rightarrow 28$ A as read on the power supply) in 1 or 2 minutes. This is too fast to obtain an undistorted spectrum but it lets us quickly find out what is happening.

4. Now sweep through the spectrum and note the positions of any signals. If the baseline is strongly sloped, maximize the microwave transmission by adjusting the microwave tuning voltage more carefully. The desired Cr^{3+} signal should be the strongest one present, and you may need to decrease the gain if its signal is too strong for convenience. Rotate the crystal a bit, maximize the diode current and sweep again in the same direction. Doing three or four orientations this way should tell you whether or not you must contend with an anisotropic spectrum.

On the basis of these measurements you have roughly characterized the problem. If indeed Cr^{3+} is in an environment with the assumed symmetry you should have a strong isotropic resonance near $g=2$ from the $I=0$ isotopes. You have probably also seen resonances from other ions which you can ignore for now. To quantify the results, proceed as follows.

1. Adjust the sweep range and lock-in gains to get a clear plot of the very strong $I=0$ component. The resonance should occupy about the middle quarter of the chart for best accuracy. Sweep the field in both directions, calibrate with NMR, and measure the microwave frequency so you can determine g for the central peak.

2. Increase the gain until you can clearly see the hyperfine lines. You are looking for four equally-spaced features relatively close to the main line. It is convenient to leave the sweep the same to avoid recalibration. Analyze the results to obtain the A parameter in Eq. 6, being careful to note that two hyperfine lines are nearly buried under the $I=0$ line. The accepted value is $A = 1.98 \times 10^{-7} \text{eV}$.

3. Measure the relative amplitude of the hyperfine lines and the main line. Use the amplitudes to estimate the ratio of ^{53}Cr to the $I=0$ isotopes. Be sure to account for the fact that the ^{53}Cr absorption is distributed across four lines while all $I=0$ absorption is in one line. Does your estimate agree with the natural abundance?

4. Overall, are your spectra consistent with the presence of Cr^{3+} and the energy level scheme of Fig. 2?

F. Cr^{3+} in Al_2O_3

The Cr^{3+} ion can also be incorporated into aluminum oxide, Al_2O_3 . Presuming that the Cr^{3+} substitutes for some of the Al^{3+} , the environment will again have approximately octahedral symmetry. Precise x-ray measurements, however, indicate that the symmetry is not perfect. Accordingly we expect the energy levels of Fig. 3 and Eq. 7 to describe this system. A full analysis to determine the parameters in Eq. 7 requires comparing a detailed calculation of expected line positions as a function of angle with spectra taken at many angles. Rather than carry out this program we will just demonstrate some of the qualitative features.

Place the $\text{Al}_2\text{O}_3\text{:Cr}^{3+}$ sample in the cavity and retune for maximum diode current. Note, incidentally, that the crystal is ruby red (pure Al_2O_3 is colorless), indicating that the optical levels of Fig. 1 must have shifted relative to MgO . Carry out the survey procedure described in the previous section to obtain a rough idea of the spectrum, keeping in mind that only the strongest lines are likely to be due to Cr.

Obtain spectra to show that absorption occurs at different fields for different sample orientations. Show that it would be possible to track individual transitions by following one or two lines as they shift in field over a few small-angle rotation steps. Discuss your main results in the context of Eq. 7.

G. EPR of "pure" MgO

The last sample is nominally pure MgO . Even though it is colorless the survey procedure will indicate strong EPR signals. Obtain good spectra for the stronger lines in this sample at one or two orientations. It is probably most useful to look first at a field range that contains all the peaks and then to magnify the amplitude and field region around one of the prominent peaks.

The objective of our qualitative analysis is a plausible identification of the residual impurities responsible for the spectrum. In a research situation the identities would be confirmed by comparing spectra from the unknown sample with spectra from deliberately doped specimens.

The argument proceeds from the chemical fact that it is difficult to completely separate the 3d elements, with an $[\text{Ar}]\text{3d}^n\text{4s}^2$ configuration, from Mg, a $[\text{Ne}]\text{3s}^2$ configuration. The impurities are likely, therefore, to be one or more 3d elements. The charge state, and hence possible crystal field splittings, are quite unknown but the nuclear parameters are fixed. Also, since the crystal is colorless the concentration must be much smaller than in the other crystals you have used. Together, these facts suggest that we can use the strength of the EPR signals along with the known nuclear spins and abundances to pick out some likely candidates. Use the table in the Appendix to choose those isotopes that could be the source of your spectra and identify the features in the spectrum that you would associate with each class of candidates. If other features would be useful in later comparisons with standard samples, point them out as

well.

Once you have tentative identifications for the contaminants in this sample, you could take another spectrum of the MgO:Cr^{3+} sample with higher gain to see if some of the same lines can be identified in that specimen. Again, the pattern of the nuclear hyperfine structure is likely to give the best clue.

IV. Appendix

Some Useful Numbers

$$h = 4.135701 \times 10^{-15} \text{ eV}\cdot\text{s}$$

$$\mu_B = 5.7883785 \times 10^{-9} \text{ eV/G}$$

$$g_e = 2.0023$$

resonant frequencies - protons: 4.25770 MHz/kG

electrons: 2.80244 GHz/kG

magnet calibration: 0.136 kG/A

Properties of 3d Isotopes

Isotope	Spin	Abundance
⁴⁵ Sc	7/2	100.%
⁴⁶ Ti, ⁴⁸ Ti, ⁵⁰ Ti	0	87.2
⁴⁷ Ti	5/2	7.3
⁴⁹ Ti	7/2	5.5
⁵¹ V	7/2	100.
⁵⁰ Cr, ⁵² Cr, ⁵⁴ Cr	0	90.5
⁵³ Cr	3/2	9.6
⁵⁵ Mn	5/2	100.
⁵⁴ Fe, ⁵⁶ Fe, ⁵⁸ Fe	0	97.8
⁵⁷ Fe	1/2	2.2
⁵⁹ Co	7/2	100.
⁵⁸ Ni, ⁶⁰ Ni, ⁶² Ni, ⁶⁴ Ni	0	98.9
⁶¹ Ni	3/2	1.2
⁶³ Cu	3/2	69.1
⁶⁵ Cu	3/2	30.9