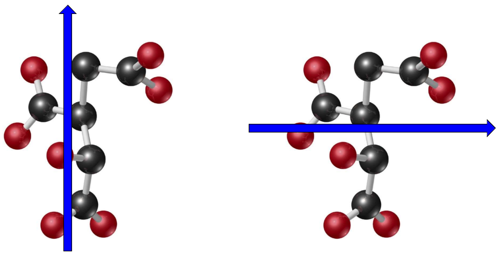
Electron Paramagnetic Resonance: molecules and solids

www. hyperfinecourse .org

What's the difference (1) ?



As soon as your sample is not a free atom any longer, there is **anisotropy**: the orientation of the applied field w.r.t. the molecule or solid matters.

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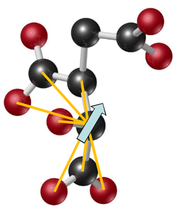
What's the difference (2) ?



The moment of the considered atom does not only interact with the external field and with the field due to its own nucleus, but also with the fields due to other nuclei and due to electrons around those other nuclei (fades out with distance).

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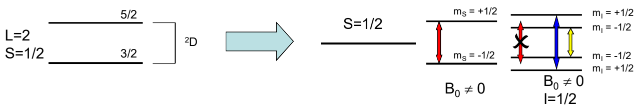
What's the difference (3) ?

Quenching of the orbital angular momentum in many solids (L≈0)



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EPR Hamiltonian for solids/molecules

$$\hat{H} = -\frac{\mu_B}{\hbar}\vec{B}_0 \cdot \overleftrightarrow{g} \cdot \vec{S} + \sum_{k=1}^{N} \frac{1}{\hbar^2} \vec{S} \cdot \overleftrightarrow{A}_k \cdot \vec{I}_k - \sum_{k=1}^{N} g_{n,k} \frac{\mu_N}{\hbar} \vec{I}_k \cdot \vec{B}_0$$

- S instead of J (quenching of L)
- no scalar g_e, but a g-matrix (or g-tensor) :

$$\overleftrightarrow{g} = \begin{bmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{bmatrix}$$

This is a Cartesian tensor, not a spherical tensor. That means the matrix need not to be symmetric, nor need the trace to be zero.

Terms with such a tensor (that is not a multiple of the unit matrix) are called **anisotropic**. Their value depends on the orientation of the applied field w.r.t. the sample. (Here: the way in which B_0 is – slightly – perturbed by internal fields depends on the orientation of B_0.)

- Even if $\overleftrightarrow{g}$ is a multiple of the unit matrix, the diagonal element might differ slightly from g_e. This reflects the fact that the field felt by the electron is not only the applied field, but a sum of applied field and local (internal) fields.

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- hyperfine coupling (=interaction between electron spin and nuclear spin)
- has an isotropic part (contact interaction and orbital interaction) and an anisotropic part (dipolar interaction).

The direction of the contact field is anisotropic, but its magnitude is not. Only the magnitude survives in the final expression.

The spatial distribution of the electrons determines the orbital field. This spatial distribution is only to a small extent affected by (the direction of) an applied field.

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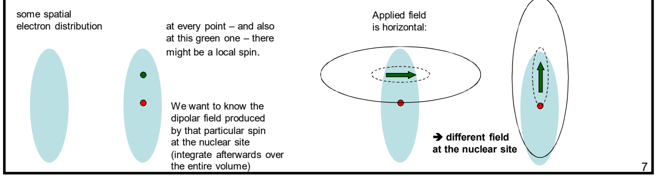
Reasoning from the point of view of the electron spin:



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EPR Hamiltonian for solids/molecules

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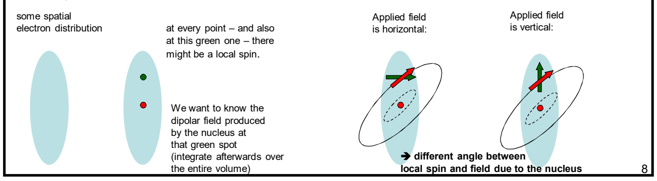
- hyperfine coupling (=interaction between electron spin and nuclear spin)
- has an isotropic part (contact interaction and orbital interaction) and an anisotropic part (dipolar interaction)

Reasoning from the point of view of the nuclear spin:



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EPR Hamiltonian for solids/molecules

$$\hat{H} = -\frac{\mu_B}{\hbar}\vec{B}_0 \cdot \overleftrightarrow{g} \cdot \vec{S} + \sum_{k=1}^{N} \frac{1}{\hbar^2} \vec{S} \cdot \overleftrightarrow{A}_k \cdot \vec{I}_k - \sum_{k=1}^{N} g_{n,k} \frac{\mu_N}{\hbar} \vec{I}_k \cdot \vec{B}_0$$

- hyperfine coupling (=interaction between electron spin and nuclear spin)
- has an isotropic part (contact interaction and orbital interaction) and an anisotropic part (dipolar interaction).
- interaction not only with the nucleus of the 'own' atom, but with all nuclei in the solid

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EPR Hamiltonian for solids/molecules

$$\hat{H} = -\frac{\mu_B}{\hbar}\vec{B}_0\cdot\overleftrightarrow{g}\cdot\vec{S} + \sum_{k=1}^{N}\frac{1}{\hbar^2}\vec{S}\cdot\overleftrightarrow{A}_k\cdot\vec{I}_k - \sum_{k=1}^{N} g_{n,k}\frac{\mu_N}{\hbar}\vec{I}_k\cdot\vec{B}_0$$

- interaction between the nuclear spins and the external field
- to a good approximation isotropic

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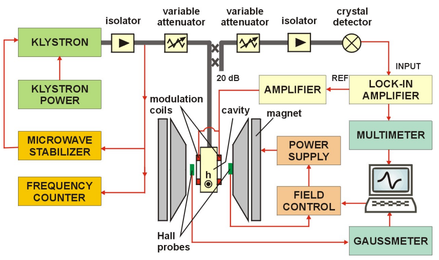
Description of a EPR spectrometer

(more or less randomly taken from the internet)



A modified Varian electron paramagnetic resonance (EPR) spectrometer is used with a klystron to do ferromagnetic resonance (FMR) spectroscopy in the X-band (9.53 GHz). The magnetic sample to be measured is placed between the poles of an electromagnet, at the end of a shorted waveguide or centered in a cavity. An incident microwave signal couples to the sample and is partially absorbed. A crystal detector then measures the reflected microwave signal. This signal from the crystal detector is then input into the lock-in amplifier where it is compared with the reference signal. The output voltage from the lock-in amplifier vs. the external magnetic field corresponds to the derivative of the absorption curve. The half power linewidth and magnetic resonance field can be then found easily.

http://www2.physics.colostate.edu/groups/PattonGroup/systems/epr_desc.html

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Two examples of EPR spectrometers. The two coils of the electromagnet are a typical feature.

(historical) example

PHYSICAL REVIEW VOLUME 138, NUMBER 2A 19 APRIL 1965

Defects in Irradiated Silicon: Electron Paramagnetic Resonance of the Divacancy

G. D. WATKINS AND J. W. CORBETT
General Electric Research Laboratory, Schenectady, New York
(Received 19 November 1964)

Context: Irradiate (doped) Si with high-energy electrons, in order to create defects. Some of these defects have unpaired electrons (=S), and therefore produce a signal in EPR experiments.

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(historical) example

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The G6 spectrum is observed in low-resistivity *p*-type silicon. In boron-, aluminum-, gallium-, or indium-doped silicon it grows linearly with irradiation dose as long as the Fermi level remains locked to the acceptor level. The production rate in a room temperature radiation at 1.5 MeV is[10] ≈0.008 defects/cm^3 per electron/cm^2 which is an order of magnitude lower than the single-vacancy production (as monitored by the oxygen-vacancy pairs).[10]

The G7 spectrum is observed in high-resistivity *n*-type silicon. Starting with phosphorus-doped silicon, these defects are not observed until the irradiation has proceeded far enough that the Fermi level has receded to $\approx (E_c - 0.4)$ eV. It is thus associated with a level at this position and is observed only when this level does not contain an electron. The production rate is therefore less easy to measure, but it appears comparable to the G6 spectrum in *p*-type material.

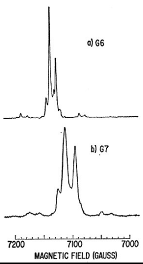

FIG. 1. Spectra at 20 kMc/sec with H$||\langle 100\rangle$ and $T = 20.4$°K.

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(historical) example

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Question: To which defects does these two EPR signals correspond ?

(EPR tells you only that these defects exist, not what they are)

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Further characterization: examine anisotropy, determine PAS of g-tensors

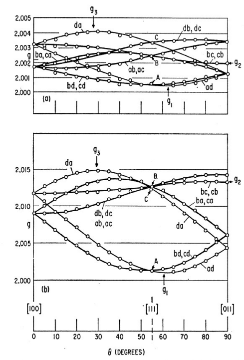
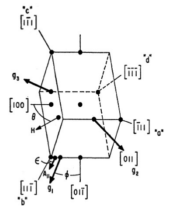


FIG. 2. g values versus crystalline orientation with **H** in the (01$\bar{1}$) plane (see Fig. 3). (a) G6 spectrum, (b) G7 spectrum.



G6: $g_1 = 2.0004 \pm .0003$, $g_2 = 2.0020 \pm .0003$, $g_3 = 2.0041 \pm .0003$, $\phi = 27.6 \pm 0.5°$; $A_{\parallel} = 67.8 \pm 0.5\ (10^{-4})\ cm^{-1}$, $A_{\perp} = 40.0 \pm 0.5\ (10^{-4})\ cm^{-1}$, $\epsilon = +0.5 \pm 0.3°$

G7: $g_1 = 2.0012 \pm .0003$, $g_2 = 2.0135 \pm .0003$, $g_3 = 2.0150 \pm .0003$, $\phi = 29 \pm 1°$; $A_{\parallel} = 79 \pm 2\ (10^{-4})\ cm^{-1}$, $A_{\perp} = 56 \pm 2\ (10^{-4})\ cm^{-1}$, $\epsilon = -2 \pm 1°$

FIG. 3. Spin-Hamiltonian constants for the G6 and G7 spectra with axes indicated for one of the twelve defect orientations in the lattice. With the magnetic field **H** in the (01$\bar{1}$) plane as shown, this set of axes gives rise to the g values given by *cb* in Fig. 2.

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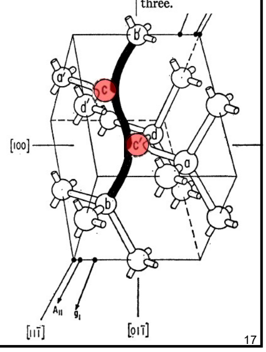
Conclusion/interpretation (based on a list of indirect evidence) :

VI. SUMMARY AND CONCLUSIONS

We conclude that the divacancy introduces a single donor and two acceptor levels into the forbidden gap and can therefore exist in four different charge states. We identify two epr spectra, G6 and G7, as arising from the singly positive and the singly negative charge states of the divacancy, respectively.

The model of the divacancy deduced from the studies in this paper is one in which the two vacancies are at adjacent atom sites. Four of the six silicon atoms adjacent to the divacancy bond together by pairs and the remaining electrons are spread over the other two atoms, which are separated from each other across the divacancy. For the G6 spectrum there is one electron shared between these two atoms; for the G7, there are three. This pulling together of the other atom pairs can be viewed as a manifestation of the Jahn-Teller effect.

FIG. 4. Model of the divacancy. The G6 spectrum arises from one electron in the extended orbital between atoms b and b'; the G7 from three.



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How to unravel such problems nowadays :

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First-Principles Theory of the EPR g Tensor in Solids: Defects in Quartz

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(Received 17 September 2001; published 11 February 2002)

A theory for the reliable prediction of the EPR g tensor for paramagnetic defects in solids is presented. It is based on density functional theory and on the gauge including projector augmented wave approach to the calculation of all-electron magnetic response. The method is validated by comparison with existing quantum chemical and experimental data for a selection of diatomic radicals. We then perform the first prediction of EPR g tensors in the solid state and find the results to be in excellent agreement with experiment for the E_1' and substitutional phosphorus defect centers in quartz.

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