6. ELECTRON PARAMAGNETIC RESONANCE

6.1 Introduction

In electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR), the resonant absorption of electromagnetic radiation by magnetic moments of unpaired electrons is measured in the presence of a static magnetic field. Electron paramagnetic resonance was discovered in 1944 by Zavoisky (Kazan State University, Russia). EPR has a wide range of applications in chemistry, physics, biology, and medicine; it may be used to probe the "static" structure of solid and liquid systems, and is also very useful for investigating dynamic processes. In the framework of this thesis it should be emphasized that EPR can also be used as a tool for dating geological samples (see e.g. Ikeya, 1993).

Application of zircon as a medium for TL dating requires detailed knowledge of the processes taking place during, for example, exposure of zircon to ionizing radiation, long-term storage, annealing, and excitation with (visible-UV) light. EPR is a powerful method for investigating the detailed physical properties of paramagnetic defects in ionic materials, including zircon. In particular, radiation-induced defects can be investigated effectively by means of EPR, because many of these defects are paramagnetic.

The presence of a multitude of paramagnetic defects in natural zircon complicates the interpretation of the EPR signal. Nevertheless, natural zircon crystals have been studied intensively with EPR, and many of the paramagnetic point defects have been identified and described. In this chapter we will study the EPR spectra of the rare-earth ions Dy$^{3+}$ and Tb$^{4+}$ and several paramagnetic SiO$_m^-$ centers, which play a key role in the damage formation and TL processes in natural zircon.

6.2 EPR theory

In EPR experiments defects are studied by observing the splitting between electron spin energy levels, which are modified by interactions of the defect with the crystal field, nuclear spins and moments and the external magnetic field. The most simple case is a free electron with spin $s = \frac{1}{2}$. In the absence of a magnetic field the magnetic moment, associated with the electron spin, is randomly oriented and the two energy levels are degenerate. An applied magnetic induction $B_0$ removes the degeneracy and splits the energy level into two levels characterized by the spin quantum numbers $m_s = \pm \frac{1}{2}$. The

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$^4$ The EPR measurements have been carried out in Groningen in collaboration with Dr's G.R. Bulka and M.A. Laruhin, Kazan State University, Russia. An extensive account of this work has been given in Laruhin et al, 2002.

$^5$ The magnetic induction is denoted by $B_0$ and is measured in tesla (T) in the SI system. However, in EPR spectroscopy the CGS unit gauss (G), where 1 G = $10^{-4}$ T, is commonly used.
splitting between the two energy states is called *electron Zeeman interaction* and is proportional to the magnetic induction (see figure 6.1a). Absorption of energy causes a transition from the lower energy to the higher energy state. The absorption frequency corresponds to the energy difference between the spin states. The frequency of electromagnetic waves may vary from e.g. the Megahertz range, via the frequencies of visible light, to those associated with ultraviolet light. Electromagnetic waves in the Gigahertz range are used for EPR experiments.

The energy difference between the two spin levels of a free electron in an external magnetic field is \( \Delta E = g\beta B_0 \), where \( g \) is called the g-factor or the spectroscopic splitting factor and \( \beta \) is the electron Bohr magneton (\( \beta = \frac{e\hbar}{2m} \)). Transitions between the two energy levels can be induced by means of an alternating electromagnetic field \( B_1 \cdot e^{i\omega t} \), with angular frequency \( \omega \), if \( \hbar \omega = g \beta B_0 \). It is possible to scan through the spectrum of energy levels by changing either the magnetic induction \( B_0 \) or the angular frequency \( \omega \). Allowed transitions obey the selection rule \( \Delta m_s = \pm 1 \).

For practical reasons in EPR measurements the transitions are measured using a frequency-controlled klystron, operating at a fixed angular frequency \( \omega \) and an external magnetic induction \( B_0 \), which varies linearly with time. The resonance condition is given by

\[
B_0 = \frac{h\omega}{g\beta}
\]  

(6.1)

The electronic energy levels may be split further by nuclear interactions when the spin quantum number \( I \) of the nucleus differs from 0 (figure 6.1b). For a given nuclear quantum

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\[ \Delta E = \hbar\omega = g\beta B_0 \]

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\( m_s = \frac{1}{2} \)

\( m_s = -\frac{1}{2} \)

\( m_I = \frac{3}{2} \)

\( m_I = \frac{1}{2} \)

\( m_I = -\frac{1}{2} \)

\( m_I = -\frac{3}{2} \)

\( + \frac{3}{2} \)

\( + \frac{1}{2} \)

\( - \frac{1}{2} \)

\( - \frac{3}{2} \)

\( + \frac{1}{2} \)

\( + \frac{3}{2} \)

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Figure 6.1. *Energy level diagram for a) a spin system with one electron \( S = \frac{1}{2} \) and b) the hyperfine line pattern produced by interaction with a nucleus of \( I = \frac{3}{2} \). In the calculation of the energy levels it was assumed that the nuclear quadrupole moment is 0.*

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6 In atomic physics the symbol \( S \) is used; in nuclear physics \( J \). We adhere to the former.
number $I$ splitting into $(2I+1)$ energy levels is observed, the levels being characterized by the nuclear spin quantum numbers $m_I = I, I-1, \ldots, -I$. The interaction of the electron spin with the nucleus is called hyperfine interaction. When the unpaired electron interacts with more than one magnetic nucleus, the energy level scheme may become very complex.

In the EPR spectrum the hyperfine lines associated with an interacting nucleus are equidistant at any particular setting of the magnetic field with respect to the defect axis. The appearance of electron nuclear interactions is very powerful for the identification of defects because in many cases one can vary the isotope concentrations of the elements in the crystal.

For a completely free electron the $g$-factor is 2.0023, which implies that at $10^{10}$ Hz (corresponding to microwaves with a wavelength of 3 cm) the magnetic induction required for resonance is 0.357 T (= 3570 Gauss).

6.3 Experimental set up and radiation facilities

The EPR measurements have been carried out with a Varian ‘E-line Centuries Series’ X-band EPR spectrometer. A gas-flow helium ESR9 ‘Oxford instruments’ cryostat has been used to stabilize the temperature with an accuracy of 0.3 K, in the range 4.2 - 300 K.

X-irradiation at room temperature has been carried out by means of an X-ray tube, with a tungsten anode, operating at 60 kV and 30 mA for several hours. A calibrated $^{137}$Cs source was used to produce $\gamma$-irradiation at room temperature with a total dose 10 kGy, at a dose rate of 2.57 Gy/min. Much higher doses (up to several 100 kGy) and much higher dose rates (typically ~ 1 MGy/h) were obtained with electrons (energy ~ 0.5 MeV, maximum current ~ 1 mA). For the exposure of the samples to these high-energy electrons we have used the linear electron accelerator at the Solid State Physics laboratory, University of Groningen.

Annealing experiments on irradiated zircon samples have been carried out in air as a function of the temperature up to 550ºC using the furnace of a Perkin Elmer DSC-7 differential scanning calorimeter, which provides controlled heating rates in the range 120-250ºC/min, and a cooling rate of 250ºC/min.

Note: The hyperfine lines are equidistant only if the external magnetic field is much larger than the hyperfine splitting parameter. If this is not the case second-order effects may be observed, and the hyperfine lines are not exactly equidistant. In addition, it should be noted that for spins with $I > 1/2$ in principle nuclear quadrupole interactions contribute to the energy of the spin. These interactions also lead to non-equidistant patterns of hyperfine lines.
6.4 EPR results

EPR measurements were made on single crystals of zircons (zircon single crystals) and zircon sand samples from various locations around the world. The single crystals used in this study were selected from samples from Harts Range (Australia) and Cambodia. The sand samples selected for our EPR investigations were from the Trail Ridge deposit (Florida, USA), and the island of Ameland (the Netherlands).

The TL signal of laboratory-irradiated mineral zircon is dominated by the rare earth impurities Dy$^{3+}$ and Tb$^{3+}$ (see chapter 5). The TL spectra of zircon sand samples have been discussed in detail in chapter 5. Between 100 and 200°C the spectra show the well-known Dy peaks at 480 and 580 nm and above 200°C the spectra are dominated by six Tb peaks located at 375, 416, 488, 545, 585, and 615 nm.

The TL output of the samples after artificial $\gamma$-irradiation of 10 kGy was measured in the temperature range 100-400°C, using a heating rate of 150°C/min. For a detailed description of the TL methodology see chapter 5. The 3D-TL spectra of crushed rock zircon samples from Harts Range and Cambodia show the two Dy peaks and a broad band of unknown origin at low temperatures and the Tb peaks at high temperatures (see figure 6.2 and Iaconni and Caruba, 1980).

6.4.1 Rare-earth impurities Dy$^{3+}$ and Tb$^{4+}$

We have investigated the radiation induced valence changes of the Dy and Tb ions and the valence changes of the irradiated samples during annealing by means of EPR, because it is well known that for rare-earth impurities these changes take place very often. Prior to irradiation, dysprosium and terbium impurities in zircon are in the trivalent state. During

![Figure 6.2. 3D-TL spectra of the crushed-rock zircon samples from a) Harts Range, Australia, and b) Cambodia, following 10 kGy of γ-radiation. The samples were collected and analyzed by J.F. Donoghue.](image)
irradiation the trivalent Dy and Tb ions are transformed to another valency. From TL experiments we know that during recombination the dysprosium and terbium ions return to the trivalent state and as a result light is emitted, which is characteristic for Dy\(^{3+}\) and Tb\(^{3+}\), respectively.

### 6.4.1.1 \(\text{Dy}^{3+}\)

Dy\(^{3+}\) has a \([\text{Xe}]4f^9\) electron configuration and a \(^6H_{15/2}\) ground state\(^8\). Ball (1971), as well as other authors in earlier papers, described the angular dependence of the EPR lines of Dy\(^{3+}\) in zircon for X- and Q-band resonance conditions (i.e. with microwave frequencies of about 10 and 35 GHz, respectively) with the following spin Hamiltonian (\(S=1/2, I=5/2\)):

\[
\hat{H} = g_\| \beta H_z S_z + g_\perp (H_x S_x + H_y S_y) + A S_z I_z + B (S_x I_x + S_y I_y). \tag{6.2}
\]

Here, the first two terms on the right-hand side describe the Zeeman interaction and the last two terms represent the hyperfine interaction, with isotropic and anisotropic hyperfine constants \(A\) and \(B\), respectively. The EPR lines associated with Dy\(^{3+}\) can only be observed at low temperatures (\(T = 4K\)). At room temperature, the EPR lines are very wide, and therefore very weak due to spin-lattice relaxation, which is, in general very fast for rare-earth impurity ions. Between successive EPR measurements at 4K it was necessary to remove the sample from the cryostat to allow exposure to ionizing radiation, fading or annealing.

Figure 6.3 shows the EPR spectra of Dy\(^{3+}\) ions before and after exposure to \(\gamma\)-radiation and after subsequent annealing at 300°C for 30 minutes. The concentration of the Dy\(^{3+}\) ions decreases drastically as a result of exposure to \(\gamma\)-radiation, which implies that the trivalent Dy-ions are transferred either to the divalent or the tetravalent state, by trapping radiation-induced electrons or holes, respectively. With EPR only Dy\(^{3+}\) can be observed (and not Dy\(^{2+}\) or Dy\(^{4+}\), due to the electronic configuration, the transitions are forbidden in EPR), which means that for Dy we can only investigate the radiation-induced reduction of the concentration of Dy\(^{3+}\) ions. Ultimately, after exposure to very high irradiation doses the EPR signal associated with Dy\(^{3+}\) disappears. During subsequent annealing the intensity of the Dy\(^{3+}\) EPR signal increases. The same behavior is observed in crystals after exposure to irradiation from the electron accelerator (up to a total dose of 200 kGy). Annealing experiments show that the radiation-induced Dy-center is stable up to approximately 80°C, and therefore we conclude that in the recombination/annealing process the Dy\(^{3+}\) center plays the role of a shallow trap (Laruhin et al, 2002).

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\(^8\) In spectroscopic notation, discrete (electronic) energy levels in a multi-electron atom are described by term values with the general form: \(2S + 1L_J\). Here \(S\) is the sum of all electron spins and \(2S + 1\) is called the “multiplicity”, i.e. the number of \(J\) values for given values of \(L\) and \(S\). \(L\) is the total quantum number \(J\) the spin-orbit coupling term, i.e. \(J = L + S\). When \(L = 0, 1, 2, 3, 4, 5, \ldots\) the atom is in an \(S, P, D, F, G, H, \ldots\) state, respectively. Dy\(^{3+}\) (\([\text{Xe}]4f^9\) electron configuration), having 5 unpaired electrons, \(S=5/2, L=5, J=S+L=15/2\), has a ground state, which is referred to as \(^6H_{15/2}\).
6.4.1.2 $\text{Tb}^{4+}$

From the point of view of dating the behavior of the terbium impurities forms the most interesting part of our EPR results, because the TL light, emitted at high temperatures, is predominantly due to Tb ions. With EPR only the tetravalent state of terbium ions ($\text{Tb}^{4+}$) can be observed (and not $\text{Tb}^{3+}$; due to the electronic configuration, the transitions are forbidden in EPR), which means that we can only investigate the changes in the concentration of the tetravalent terbium ions after exposure to $\gamma$-radiation and after subsequent annealing experiments and fading experiments.

$\text{Tb}^{4+}$ has a $4f^7$ electron configuration and a $^8S_{7/2}$ ground state\(^9\), which is the same as for $\text{Gd}^{3+}$ and $\text{Eu}^{2+}$. The $\text{Tb}^{4+}$ ion has a half-filled $4f$ shell, which has spherical symmetry, like noble gas atoms, and this property ensures the high stability of $\text{Tb}^{4+}$. The first studies of EPR on

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\(^9\) $\text{Tb}^{4+}$ has a half-filled f-shell, therefore $S=7/2$, $L=0$, $J=7/2$, i.e. the ground state can be written as $^8S_{7/2}$.  


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Figure 6.3. EPR spectra of Dy$^{3+}$ ions in a natural zircon single crystal from Harts Range (Australia).
Tb$^{4+}$ were made for the cubic crystal structures of ThO$_2$ and GeO$_2$, where the Tb$^{4+}$ ions are situated at sites with cubic symmetry (Baker et al., 1965, Greznev et al., 1966). The first EPR investigation of Tb$^{4+}$ ions at tetragonal sites has been carried out with zircon crystals (Hutton and Melhe, 1969).

In figure 6.4 we show the EPR spectra of Tb$^{4+}$ before and after exposure to γ-radiation and after subsequent annealing at 150, 450, and 550°C. The EPR spectrum of Tb$^{4+}$ shows four hyperfine lines ($^{159}$Tb$^{4+}$, $I=3/2$, natural abundance 100%). The EPR lines associated with Tb$^{4+}$ can be observed at T = 50 K and lower. This is because the orbital angular momentum is 0, and the spin-orbit coupling is rather weak and therefore, the spin-lattice relaxation time is long compared with many other rare-earth ions, including Dy$^{3+}$. Between successive EPR experiments at 50 K we had to remove the sample from the cryostat to allow exposure to ionizing irradiation, and perform fading or annealing experiments. The EPR line at 650 Gauss is associated with the MgO:Cr$^{3+}$ reference sample. From figure 6.4 we can see, by

**Figure 6.4. EPR spectra of a natural zircon single crystal from Harts Range.** The sample was annealed after γ-radiation at 150, 450, and 550°C for 30 minutes. Due to technical problems, a part of the line “before irradiation” is missing.
comparing the intensity of the EPR signal with the one associated with the MgO:Cr$^{3+}$ sample, that the concentration of Tb$^{3+}$ increases during $\gamma$-irradiation. Subsequent annealing leads to a decrease of the intensity of the Tb$^{4+}$ EPR lines and ultimately at temperatures higher than 550°C the signal disappears completely. This implies that above 550°C all terbium ions are transformed to the trivalent state. Similar experiments have been carried out after X- and electron beam irradiation with essentially the same results.

We assume a similar charge transfer behavior for the rare-earth ions Dy and Tb during (i) irradiation and (ii) annealing and fading. Our results indicate that during irradiation the trivalent Dy and Tb ions change to the tetravalent state. During annealing at moderate temperatures the reaction Dy$^{4+} \rightarrow$ Dy$^{3+}$ takes place and at higher temperatures the reaction Tb$^{4+} \rightarrow$ Tb$^{3+}$ is the important one. This is consistent with the TL results, showing luminescence, which is characteristic for Dy$^{3+}$ (for T between 100-200°C) and Tb$^{3+}$ (for T > 200°C). Therefore we conclude that (i) the Dy ions act as shallow hole-traps and (ii) the Tb ions act as deep hole-traps in zircon (Laruhin et al, 2002).

Saturation of the formation of Tb$^{4+}$ as a function of the irradiation dose

For the development of a reliable dating method we need information about the saturation behavior of the defect concentration as a function of the irradiation dose. For example, a typical natural zircon crystal collects an internal radiation dose from the naturally occurring radionuclides uranium and thorium (see chapter 3) of about 10 kGy during a period of approximately 13 ka. It will be interesting to know at what dose the defect levels start to saturate.

We have irradiated the same zircon mono-crystal up to various doses (with a fixed dose rate of 13 kGy/min) using an electron accelerator. After each irradiation run we completely annealed the sample at T = 550°C to bring the system back to its initial state. In figure 6.5 we show the concentration of Tb$^{4+}$ centers in the zircon sample as a function of the irradiation dose. The solid line in figure 6.5 represents the calculated dose dependence of the Tb$^{4+}$ concentration in zircon (see also chapter 7). In the next chapter we will show that with this model we are able to describe realistically the processes taking place during the excitation stage, i.e. during exposure to ionizing radiation. From figure 6.5 it is clear that saturation of the Tb$^{4+}$ concentration becomes significant for doses D > 100 kGy, i.e. almost all Tb$^{4+}$ centers are transformed into Tb$^{3+}$. It should be noted, however, that it can be expected that the saturation behavior depends on the dose rate. Further experiments to establish the dose rate effects should be carried out in the future. This result suggests that in principle TL dating with zircon can be applied to sediments in a wide range of depositional ages, probably up to more than hundred thousand years.

In the literature the saturation dose for zircon has been estimated to be at least $10^5$ Gy (Sutton and Zimmerman, 1976). This value agrees with the calculated behavior of the TL signal as a function of the dose (see chapter 7) showing that, just as we have observed in figure 6.5, saturation does not occur below $10^5$ Gy.
Figure 6.5. The concentration of Tb$^{4+}$ centers plotted in arbitrary units (a.u., proportional to the intensity of the EPR lines) in zircon versus the irradiation dose. Saturation of the Tb$^{4+}$ concentration starts at a dose $> 100$ kGy. The solid line represents the dose dependence of the Tb$^{4+}$ concentration calculated numerically with the kinetic model discussed in chapter 7. The uncertainties in the data points are due to the uncertainties in the measurements.

An important consequence is that by using the plot of Zimmerman (1972), showing the relative $\alpha$-efficiency as a function of the saturation dose (see figure 6.6), we find that the efficiency of alpha particles to produce TL in zircon is the same as for a beta source. From figure 6.6 it can also be observed that quartz has an extremely low saturation dose; correspondingly, the $\alpha$-efficiency for quartz is very low, between 2% for the 110°C TL peak and 10% for the 300°C TL peak.
In addition to the ions of the rare-earth elements Dy and Tb, an important group of paramagnetic radiation-induced defects in zircon, which can be characterized by SiO$_{n}^m$ centers, has been identified and investigated. Depending on the values of the integers $n$ and $m$, we are dealing with either electron- or hole-centers. Most of the EPR lines associated with SiO$_{n}^m$ centers in natural zircons (i.e. non-irradiated zircons) are too weak to be characterized and assigned to particular defect centers. We have irradiated the samples in the laboratory with X-rays, $\gamma$-radiation, or electrons from an electron accelerator in order to increase the concentrations of the radiation induced defects centers to sufficient levels to study the effect of irradiation on the defect concentration and the thermostability of the centers.

In figure 6.7 we show a typical EPR spectrum of a zircon single crystal from Harts Range (Australia) measured at room temperature after exposure to $\gamma$-radiation (10 kGy). The EPR line of Gd$^{3+}$ is observed in zircon crystals from all sample locations and it is relatively strong in a wide range of temperatures, including room temperature. This property is very useful for the purpose of obtaining the precise orientation of the axes of the crystalline samples with respect to the direction of the static magnetic field. This signal has also been
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used to find the positions of the EPR lines of the radiation-induced signals and this has helped us to define the principal values of the magnetic parameters of the defects.

The EPR lines of Cr$^{3+}$ and Mn$^{2+}$ are from the MgO calibration sample with well-known $g$-factors, which is placed in the EPR cavity together with the zircon sample. These lines allow us to calculate the klystron frequency, if the magnetic field is known.

For the identification of the centers we have studied the angular dependence of the EPR lines in the important crystallographic planes. As an example we show in figure 6.8 the behavior of the resonance lines in the vicinity of $g=2$ during rotation of the crystal with respect to the external magnetic field. In figure 6.8 the direction of the magnetic induction is perpendicular to the crystallographic [010] axis. The angular dependence was examined to calculate the $g$-tensor parameters. The position of one of the EPR lines in figure 6.8 does not depend on the orientation of the magnetic induction with respect to the crystallographic axes. The corresponding $g$-factor is isotropic (independent of sample orientation in a magnetic field), because also in the other planes of rotation the same independent behavior is observed; it is found to be $2.000 \pm 0.001$. This behavior is characteristic for the SiO$_4^{5-}$

Figure 6.7. EPR spectrum of several SiO$_m^{n-}$ ion-radicals (measured at room temperature) in a $\gamma$-irradiated zircon single-crystal from Harts Range, Australia, B||[001].

The EPR lines of Cr$^{3+}$ and Mn$^{2+}$ are from the MgO calibration sample with well-known $g$-factors, which is placed in the EPR cavity together with the zircon sample. These lines allow us to calculate the klystron frequency, if the magnetic field is known.
center, which is formed during exposure of the zircon sample to ionizing radiation (Solntsev et al., 1974). The SiO$_4^{5-}$ center, identified as an electron-center, consists of an electron trapped by a host SiO$_4^{4-}$ molecular ion, which is present in very large numbers. In this respect the SiO$_4^{5-}$ center is different from all other centers studied in this investigation.

Another defect, which appears in the crystal after exposure to ionizing radiation, is the SiO$_3^{3-}$ center (see figure 6.7). This defect shows EPR lines, which depend on the orientation of the sample with respect to the static magnetic field (figure 6.7). For an arbitrary orientation of the sample in the magnetic field this center shows four lines. The principal g-values are $g_X = g_Y = 2.0110$ and $g_Z = 2.0011$. It should be noted that in general the principle axes of the defect don’t coincide with the main crystallographic axes of zircon. The g-values along the crystal axes are $g_{[001]} = 2.0025$ and $g_{[100]} = 2.0098$. The above-mentioned parameters are similar to the g-values of the SiO$_2^{3-}$ + Y$^{3+}$ defect, described by Nizamutdinov (1976), with principal g-values $g_X = 2.0033$, $g_Y = 2.0076$ and $g_Z = 2.0168$. The g-factor provides information about the nature of the defects and it tells us whether it is an electron-
or a hole-center. When \( g > 2.0023 \) it is usually a hole-center, and when \( g < 2.0023 \) it is an electron center. In accordance with the EPR data we conclude that the \( \text{SiO}_2^{3-} \) center is a hole-type defect. EPR spectra with approximately the same properties have been found for another hole-type defect, labeled \( \text{SiO}_2^+ \) (II). It should be noted that not in all samples \( \text{SiO}_2^+ \) (II) centers are produced, which indicates that these centers are probably non-intrinsic, radiation-induced defects. This is in agreement with the interpretation given by Nizamutdinov (1976) in terms of combined defects consisting of \( \text{SiO}_2^{3-} \) and a \( \text{Y}^{3+} \) impurity.

The \( \text{SiO}_4^{5-} \) center in zircon sand samples

As described above, the position of the EPR line of the \( \text{SiO}_4^{5-} \) center is independent of the orientation of the magnetic field, i.e. the signal is isotropic. As a result of this property, the \( \text{SiO}_4^{5-} \) center can be detected in single crystals as well as in powders. This also means that this center can be investigated easily in single crystals with random orientations and concentrates of zircon from sediment samples, and it enables us to investigate these defects in zircon sand samples with grain sizes smaller than 100 \( \mu \text{m} \), whereas the \( \text{Dy}^{3+} \) and \( \text{Tb}^{3+} \) centers have only been detected in zircon monocrystals.

Figure 6.9 shows the EPR spectra of a zircon sand sample from the Trail Ridge deposit (Florida, USA). The natural zircon sand sample, which has not been irradiated in the laboratory, contains a detectable number of \( \text{SiO}_4^{5-} \) centers (figure 6.9a). Exposure of the sample to \( \gamma \)-radiation leads to an increase of the intensity of the EPR line associated with the \( \text{SiO}_4^{5-} \) center (figure 6.9b). After storage in the dark for 6 months at room temperature, the EPR signal due to \( \text{SiO}_4^{5-} \) centers has faded slightly, but it is still rather intense (figure 6.9c).

In figure 6.9 the EPR lines associated with the \( \text{Ti}^{3+} \) center can also be observed, because titanium is one of the many impurity ions in zircon. It should be noted that even though the EPR spectrum of the axially symmetric \( \text{Ti}^{3+} \) center in zircon is anisotropic, still two resonance lines can be observed. These lines are asymmetric and do not look like the first derivative of a Gaussian or Lorentzian resonance line. The \( \text{Ti}^{3+} \) peaks can be explained by a summation of the resonance lines associated with all orientations of the powdered sample with respect to the magnetic field direction. As a result two resonance phenomena are observed, which are located at positions in accordance with the principle values of the \( g \)-tensor, i.e. \( g_{//} \) and \( g_{\perp} \).
From our TL experiments we know that storage of irradiated samples in the dark at room temperature leads to a decrease of the concentration of several types of defects (fading). To obtain more information about the fading process, we have studied the thermal stability of the paramagnetic SiO$_{2-}^{5-}$, SiO$_{2-}^{3-}$ (II), and SiO$_{4-}^{5-}$ centers in zircon crystals. Figure 6.10 shows the EPR results of a natural Harts Range zircon single crystal (i.e. before $\gamma$-irradiation), after $\gamma$-irradiation and after storage in the dark for six months at room temperature following exposure to $\gamma$-irradiation. From figure 6.10 we can see that by...
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comparing the intensity of the EPR signal of the SiO$_2^-$ center with the line associated with Gd$^{3+}$, the intensity of the SiO$_2^-$ center increases during irradiation and decreases slightly when the sample is kept in the dark at room temperature. The result shows that at room temperature in irradiated zircon samples significant fading of the SiO$_2^-$ centers takes place.

The intensity of the SiO$_2^-$ center does not decrease appreciably, i.e. at room temperature the SiO$_4^{5-}$ center is reasonably stable. The natural zircon crystal contains detectable numbers of SiO$_2^-$ centers and the irradiated sample shows a rather intense signal due to SiO$_4^{5-}$ centers. Even after storage of the sample in the dark for six months the reduction of the concentration of SiO$_4^{5-}$ centers is very limited.

![EPR spectra of a zircon single-crystal from Harts Range (Australia), B || [001]. a) a natural zircon single crystal without preliminary annealing; b) after exposure to γ-radiation; c) after storage in the dark for six months at room temperature following exposure to γ-radiation.](image)

Figure 6.10. EPR spectra of a zircon single-crystal from Harts Range (Australia), B || [001]. a) a natural zircon single crystal without preliminary annealing; b) after exposure to γ-radiation; c) after storage in the dark for six months at room temperature following exposure to γ-radiation.
Our results show that the SiO$_{4}^{5-}$ center is an important defect, because it acts as a source of the electrons needed for recombination, which is the key process in luminescence dating. Figure 6.11 shows the behavior of the SiO$_{4}^{5-}$ center during heating of a crushed rock sample from Harts Range (Australia) after $\gamma$-irradiation. In this figure the integrated intensity of the SiO$_{4}^{5-}$ peak after annealing is shown as a function of the annealing temperature. From figure 6.11 it is clear that with increasing annealing temperature the intensity of the EPR line of the SiO$_{4}^{5-}$ center decreases. Between 400 and 450°C the signal decreases very rapidly with increasing temperature. This demonstrates that the SiO$_{4}^{5-}$ center loses an electron during heating as a result of recombination, because this process takes place in the same temperature interval as TL. The results presented in figure 6.11 also demonstrate that the SiO$_{4}^{5-}$ center is far more stable than the shallow trap systems SiO$_{2}^{3-}$ and Dy$^{4+}$ (see figures 6.12 and 6.14). The behavior of SiO$_{4}^{5-}$ centers is crucial for modeling TL related processes in zircon, because they are involved in many of the defect related and recombination processes at moderate and high temperatures.

![Graph showing integrated EPR intensity of the SiO$_{4}^{5-}$ line as a function of annealing temperature.](image)

Figure 6.11. The integrated EPR intensity of the SiO$_{4}^{5-}$ line of a $\gamma$-irradiated crushed rock zircon sample from Harts Range (Australia) as a function of the annealing temperature.

### 6.5 Kinetics of paramagnetic centers in zircon

For the evaluation of the parameters, which are relevant for the kinetics (evolution) of the centers studied in this chapter, we have performed annealing experiments for some of the paramagnetic centers in irradiated zircon as a function of the temperature.
The annealing experiments have been carried out in a computer controlled DSC oven as a function of the temperature up to 550ºC. In figure 6.12 we show the effects of annealing on the behavior of $\text{SiO}_2^{3-}$ centers in a zircon single-crystal after exposure to $\gamma$-irradiation. From figure 6.12 it can be seen that annealing results in a rapid decrease of the concentration of the $\text{SiO}_2^{3-}$ centers, as a result of the small trap depth of these centers. The $\text{SiO}_2^{3-}$ centers have a strongly reduced stability at temperatures higher than 200ºC. Annealing for five min. at 200ºC is sufficient to completely diminish the EPR intensity of these defects.

Remarkably, a comparison with figure 6.13 shows that the $\text{SiO}_2^{3-}$ centers are much less stable than the $\text{SiO}_2^{2-}$ (II) centers. The reason for this is still unknown.

For the development of a kinetic model, used to simulate the processes taking place at the various relevant stages of thermoluminescence dating, we need information about the annealing kinetics of the trapping centers. This will be used as input information for the kinetic model, which will be discussed in chapter 7.
SiO$_2^{3-}$ centers

We have observed that the SiO$_2^{3-}$ hole-centers are not stable at temperatures higher than 120ºC. The EPR signal associated with this center disappears completely during annealing at temperatures above 100-120ºC. In figure 6.12 we show the EPR intensity of the SiO$_2^{3-}$ center versus the annealing time measured at room temperature, after annealing for 5 minutes between 70 and 80ºC. Between successive EPR experiments the sample was removed from the cavity to anneal it for 5 minutes in the DSC oven.

The detailed annealing behavior of these centers cannot be described by a simple exponential law corresponding to one well-defined shallow trap. This means that several centers are involved in the annealing process. The behavior of the electron- and hole-centers is strongly coupled due to interaction, and the excitation of electron-hole pairs, trapping of free electrons and holes, redistribution of electrons and holes over the available traps by ionization and because subsequent re-trapping and recombination processes occur simultaneously. In fact, the situation in zircon is quite complex, because we have to take into account the effects of at least three hole-traps (Dy$^{3+}$, Tb$^{3+}$, and SiO$_2^{3-}$). In addition, we assume that there are several electron traps with different trap depths.

SiO$_2^{3-}$ (II) centers

The SiO$_2^{3-}$ (II) center is more stable than the SiO$_2^{3-}$ center. In figure 6.13 we show the dependence of the EPR intensity associated with the SiO$_2^{3-}$ (II) center versus the annealing time for three annealing temperatures (180, 190, and 200ºC). From a comparison of figures 6.12 and 6.13 it clear that for SiO$_2^{3-}$ (II) centers higher temperatures are needed to obtain the same fading of the EPR signal as for the SiO$_2^{3-}$ center. This proves that the SiO$_2^{3-}$ (II) center has a significantly higher stability than the SiO$_2^{3-}$ center.

Again, we have used here the theoretical model to explain the experimentally observed annealing results for the SiO$_2^{3-}$ (II) center. The curves in figure 6.13 represent the best fits of the model calculations to the experimental data. The theoretical simulations of the kinetics of the SiO$_2^{3-}$ (II) hole-type center show that the activation energy (i.e. trap depth) of this defect is 1.52 eV.
The rare-earth impurities Dy$^{3+}$ and Tb$^{4+}$

In addition to the annealing properties of SiO$_2$– (II) centers we have studied the annealing properties of the EPR signal of the rare-earth centers Dy$^{3+}$ and Tb$^{4+}$ in zircon single crystals. These centers play an important role in the TL process (see chapter 5). In figure 6.14 we show the time-dependence of the relative intensity of the EPR signal for the Dy$^{3+}$ center for annealing temperatures of 80, 90, and 100°C. Here too, the decay curves do not behave according to a single exponential decay. With the model described in chapter 7 we have calculated an activation energy of $\sim$1.2 eV, which means that for temperatures as low as 80-100°C fading occurs quite rapidly, indicating that the trivalent dysprosium impurities in zircon act as shallow hole-traps.
A different behavior is found for the Tb$^{4+}$. The EPR intensity starts to decrease at about $T \sim 300^\circ$C, but after annealing at much higher temperatures, and even up to $\sim 450^\circ$C the signal is still present to some extent. The only explanation, that we can provide, is that the Tb$^{4+}$ ion is a very deep hole-trap and the decrease of the EPR intensity is caused by recombination of this trap with electrons released from electron-traps connected to other impurities in the crystal. This means that we cannot measure the activation energy $E_a$ of the paramagnetic Tb$^{4+}$ center itself, but obtain some sort of effective activation energy $E_{a,\text{eff}}$ of an annealing process, which depends almost completely on the availability of electrons released from many other centers in the crystal.

We conclude that Tb ions in zircon act as deep hole-traps and find that the Tb$^{4+}$ concentration saturates at very high doses ($D > 100$ kGy). This result is important, because in order to avoid problems with dating due to fading we need to use the most stable part of the TL spectrum (see chapter 5), i.e. the 545 nm Tb$^{3+}$ line. The results in figure 6.5 show that TL dating with 545 nm luminescence of Tb$^{3+}$ can be used for samples older than 100,000 years.

In addition, several SiO$_m^{n-}$ centers have been studied in natural and $\gamma$-irradiated zircon single crystals and sand samples. We have found that the SiO$_3^{2-}$ centers play the role of
shallow hole-traps. The SiO$_4^{5-}$ centers are the most interesting ones because this center is produced as a result of electron trapping by highly abundant host molecular ions of the type SiO$_4^{3+}$. It is reasonably stable, its EPR spectrum is isotropic, and as a result of this property, the center is observed conveniently in natural and $\gamma$-irradiated sand samples.

These results are important because we have unraveled several of the major processes taking place in TL dating. With this new information we have been able to test and improve the theoretical model, which will be discussed in chapter 7.

6.6 Summary

In conclusion we can state that the EPR results have helped us to understand the behavior of the defect system in irradiated natural zircon during: (a) exposure to ionizing radiation, (b) fading (i.e. long-term storage following exposure to ionizing radiation in darkness at room temperature), and (c) annealing at moderate and high temperatures. Our EPR results definitely support the description of the defect system in the framework of the simulation model (see chapter 7). On the basis of our observations we conclude that

1. Saturation of defect formation in zircon as a function of the irradiation dose takes place at very high doses ($>10^5$ Gy) compared with for example quartz, where the TL intensity saturates for doses well below $10^3$ Gy. This finding underscores the utility of zircon as a Quaternary dating medium.

2. Rare-earth impurities in zircon play a role as hole-traps with depths, which depend on the rare-earth ion. In principle all rare-earth ions are present (see chapter 5) and therefore play a role in the hole-trapping and de-trapping processes and in electron-hole recombination in zircon.

3. In this thesis we have investigated only the behavior of the rare-earth TL activator ions Dy$^{3+}$ and Tb$^{3+}$. Trivalent Dy ions act as shallow hole-traps, showing rapid fading and TL emission at low temperatures. Trivalent Tb ions are deep hole-traps showing unimportant fading and prominent TL at high temperatures.

4. In addition to the hole-traps associated with rare-earth ions there are at least two more hole-traps giving rise to trapped holes of the type SiO$_4^{n-}$, one of which being very shallow (the SiO$_4^{3-}$ center), while the second one is significantly more stable (the SiO$_4^{2-}$ (II) center).

5. An important counterpart of the hole-traps mentioned in 2 and 3 is the SiO$_4^{3+}$ host molecular ion, which acts as an electron-trap. Electron-trapping leads to the formation of paramagnetic SiO$_4^{3-}$ centers with reasonably high stability.

6. The isotropic nature of the SiO$_4^{3-}$ centers in zircon and the reasonably high stability of these defects are favorable properties for EPR dating.
REFERENCES