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Interaction with Matter of Ionizing Radiation and Radiation Damages (Radicals)

Betül Çalişkan and Ali Cengiz Çalişkan

Additional information is available at the end of the chapter

Abstract

Interaction of matter with "ionizing radiation," that is, high-energy electromagnetic radiation (X- or gamma rays) or α- or β-particles, can promote chemical change which commonly involves free radicals. Free radicals formed by high-energy radiation in solids can then be identified by analysis of their EPR spectra.

Keywords: ionizing radiation, radical, radiation chemistry, radiation damage center, electron paramagnetic resonance (EPR)

1. Introduction

The interaction of ionized radiation with matter brings some changes in matter. These changes are called the radical or the radiation damage centers. Among the methods of radical formation in matter structure, ionizing radiation plays an important role. In addition to ionizing radiation, the chemical reactions and the thermal effects can also lead to radical formation. There are three different applications for radical formation:

a. irradiation (photolysis and radiolysis),

b. thermolysis (thermal homolysis),

c. redox processes (oxidation-reduction reactions) [1, 2].

In irradiative processes, the energy required to form radicals is generated either by **electromagnetic radiation (ultraviolet (UV) or visible light, X-rays, etc.)** or by **particle radiation**

(high-energy electrons; α, β, γ particles; neutrons; protons; etc.). Processes involving light absorption are called photochemistry [1]. Deterioration of the structure of the material by light effect is called photolysis. Deterioration of the structure of the material exposed to ionizing radiation is called radiolysis.

The electron paramagnetic resonance (EPR) method is used for the investigation of the radiation damage centers, which occur in the structure of the material. The breakage in the structure of the material allows the material to become paramagnetic. The paramagnetic centers are determined by EPR spectroscopy.

Much work has been done on the interaction of organic and inorganic materials with ionizing radiation. Most of these studies are on EPR [3, 4]. Generally, EPR works with gamma rays, which have the highest energy radiation [5–7].

The aim of the chapter is to recognize the types of radiation, to group the charged or uncharged particles in the ionized radiation group, and to focus on the EPR method, which will examine their effect on matter. High-energy energetic gamma and X-rays cause permanent damage to the material. They constitute defects in chemical structure. These disorders are often referred to as paramagnetic centers or radiation damage centers. Radiation damage centers are seen as free radicals in the form of breaking bonds in the structure and as anion or cation radicals in the form of electron exchange. The EPR method is used to investigate such impairments or paramagnetic centers occurring in structures of organic or inorganic materials. In this chapter, the effects of ionizing radiation on the substance will be analyzed using the EPR method.

2. Interaction with matter of ionizing radiation and radiation damages (radicals)

2.1. Ionizing radiation

Ionizing or high-energy radiation devices can be examined in three groups [8–10]:

a. charged particle accelerators (X-ray generators, medium-energy electron accelerators, and Van der Graaff accelerator),

b. radioisotope sources (^{60}Co beam source, ^{137}Cs beam source, and spent fuel elements),

c. nuclear reactor (mixed radiation of gamma quantum and neutrons). Since the ^{60}Co beam source is easily controlled [11, 12], it is more preferred.

Reactive radicals can be formed by the effect of ionizing radiation [13]. Radiation breaks bonds between atoms in molecules. The deterioration of the bonds occurs in two ways. If the bonds are broken **homolytically (paramagnetic)**, **free radicals** will form. If the bonds are broken **heterolytically (diamagnetic)**, **ionic fragments** are formed [14].

Certain types of low-energy radiation, such as ultraviolet light, may also cause ionization. Such radiation is not from the ionizing radiation group. The lowest energy limit for ionizing radiation is around 10 keV.

Charged particles are a **directly ionizing radiation** group. These particles include **energetic electrons (negatrons)**, **positrons**, **protons**, **alpha particles**, **charged mesons**, **muons**, and **heavy ions** (**ionizing atoms**). This type of ionizing radiation interacts primarily with matter via the Coulomb force. Particles push or attract electrons from atoms and molecules due to their charge.

Uncharged particles form an **indirectly ionizing radiation** group. Best examples for indirectly ionizing radiation type are **photons above 10 keV** (**X-rays** and **gamma rays**) and **all neutrons**.

Interaction of X-ray and gamma ray photons with matter causes ionization. This process is mainly in three different ways:

a. **Low-energy photons** give all their energy to an electron, which causes the electrons to break apart from atoms or molecules. This type of interaction is called **photoelectric interaction**. The photon then disappears from the medium.

b. **Intermediate-energy photons** interact with electrons as a result of the **Compton event**. Photons and electrons are scattered in different directions.

c. **Photons with more than 1.02 MeV of energy** are affected by pair production. (At around 1.02 MeV, the Compton effect continues, but the pair production is more effective.) As a result, the photon disappears and an electron-positron pair forms (due to momentum and energy conservation, this event occurs near a nucleus). The total kinetic energy of the electron-positron couple is equal to the photon energy, which is lower than the sum of and the rest-mass energies of the electron and the positron (1.02 MeV). These electrons and positrons act as **directly ionizing radiation**. As the positron continues its path, it loses its kinetic energy. As a result, they encounter an electron and destroy each other (the pair disappears). As a result of the pair production, two gamma photons come to the foreground. The two photons, which usually have an energy of 0.511 MeV, spread out to form an angle of 180° with each other.

A photon can enter into interaction with any of these events. However, more than 1022 MeV of energetic photons are required for double formation. The determination of the type of interaction depends on the energy of the photon and the material the photon interacts with.

Interaction of the material with the neutron causes inelastic collisions. These are listed as neutron capture (or activation) and fission. Both interactions are nuclear interactions. A nucleus that collides inelastically with the neutron is excited at a higher energy level. This energy is thrown from the nucleus in three ways:

a. as a gamma ray,

b. as a beta particle,

c. as both a gamma ray and a beta particle.

In the neutron capture, the interacting nucleus absorbs the neutron. After all, the energy from the nucleus goes away in four ways:

a. as a gamma ray,

b. as an X-ray,

c. as a beta particle,

d. by publishing both the gamma ray/X-ray and the beta particle.

Secondary particles cause ionization. If a heavy nucleus absorbs the neutron, then **the fission event** occurs. This may result in two lighter nuclei with radioactive character.

The radiation weighting factor (w_R) is a number that represents the value of **the relative biological effectiveness (RBE)** of the radiation. **The w_R values** are related to **linear energy transfer (LET)** and are given in **Table 1**.

The relative biological activity (RBE) of a radiation type is defined as the inverse ratio of radiation absorption doses that produce biological effects at the same amount. The stochastic biological effect is a biological effect that is caused by ionizing radiation. The higher the dose, the greater the effect. However, this increase does not follow a certain proportion with the absorbed dose. It is a totally independent biological effect. An important example of the stochastic biological effect is cancer.

The tissue weighting factor (w_T) represents the total loss in tissue or organs due to the stochastic effect caused by irradiation of the whole body. Irritation damages tissues or organs. A uniform equivalent dose applied over the entire body should be equal to the number of doses administered separately for all tissues and organs of the body [15].

2.2. Interaction with matter of ionizing radiation and radiation damages (radicals)

The separation of chemical bonds with radiation is one of the most common and direct methods that can be used to produce molecular fragments and free radicals. Ultraviolet, X- or, gamma

Type and energy range	w_R
Photons, all energies	1
Electrons and muons, all energies[2]	1
Neutrons, energy <10 keV	5
10–100 keV	10
>100 keV–2 MeV	20
>2–20 MeV	10
>20 MeV	5
Protons, other than recoil protons, energy >2 MeV	5
Alpha particles, fission fragments, heavy nuclei	20

[1]All values relate to the radiation incident on the body or, for internal sources, emitted from the source.
[2]Excluding Auger electrons emitted from nuclei bound to DNA.

Table 1. Radiation weighting factors w_R[1].

rays can break the bonds between atoms. The minimum energy required depends on the strength of the bond. The bond strength is usually about 10 eV. This value corresponds approximately to the wavelengths in the ultraviolet region. Therefore, UV region is the lowest-energy region required for free radical formation.

X- or gamma ray radiation occurs at very high values. When many solids in amorphous or crystalline form are exposed to X- or gamma rays, a large number of bonds can be broken. Thus, the free radical spectrum can be seen. Such high-energy radiation often produces **high free radical concentrations**. The electron spin (paramagnetic) resonance spectra of the radicals resulting from the high-energy irradiation have high signal-to-noise ratios as a function. However, it is difficult to say that there is a precise mechanism as a free radical production method, because there are many different types of damage.

In all irradiation experiments, it is usually necessary to use the capture mechanism to collect a large concentration of radicals. Examination of the dynamic concentration of radicals in the solution by X-ray or UV irradiation should normally be possible. The concentration at any time is determined by a balance between the rate of formation and the recombination rate. X- or gamma ray irradiation provides sufficient kinetic energy to move away from the site of molecular fragment or broken bonds at a certain speed. Thus, molecular fragments and broken bonds are trapped in the solid to prevent recombination at a sufficient distance. As a result, radicals can occur only in a viscous or a rigid solid phase and can be trapped. In ultraviolet irradiation, fragments or radicals obtained have a high rate of recombination since they do not have excess kinetic energy after bond breaking. Therefore, trapping is less likely to occur.

The results obtained by ultraviolet irradiation method will be discussed first. X- or gamma ray irradiation method will be examined in terms of "organic" and "inorganic" compounds. It should be assumed that the radiation of interest completely releases the chemical bond and leaves two molecules of an electron containing an unpaired electron. Apart from bond breakage, the bond excitation state deals with the "triplet state" which is guided in the same direction, instead of breaking into a higher-energy level by reversing one of the bond electrons.

2.2.1. Ultraviolet irradiation

Ingram et al. [16] obtained the first electron paramagnetic resonance spectra of active radicals formed by ultraviolet irradiation and trapped at low temperatures. In the experiments, the compounds to be photolyzed are dissolved in various hydrocarbons and frozen to form solid glasses at liquid nitrogen temperatures. The viscosity of the resulting glass is an important parameter. After formation, there must be a structure with little rigidity that will not prevent the radicals from moving away from where they are. On the other hand, it must have a solid structure at the level that will prevent the deterioration of radical structure. Glass can be used at room temperature for such a trapping operation. Such experiments, which lead to the formation of stable radicals in plastic films, have been performed by Bijl and Rose-Innes [17].

The glass-trapping technique at low temperature was used in the studies by Lewis and Lipkin [18], which study reactive molecules, and Norman and Porter [19], who detect free radicals trapped by UV absorption spectroscopy. However, it has been shown that the glass required

for UV is also suitable for electron resonance studies, since the small defects that will scatter the UV wavelengths badly have no effect on the microwave radiation.

2.2.1.1. Secondary radicals

In such experiments, it has been observed that secondary radicals occur frequently when radicals are produced by photolysis by reacting with solvent molecules [20]. Hydroxyl radicals are derived from **hydrogen peroxide**. These radicals are very reactive. When a small amount of hydrogen peroxide is added to the hydrocarbon glass, secondary radicals are usually obtained by proton removal from the hydrocarbons. **OH radicals** were obtained by removal of an α-hydrogen from the isopropanol molecule via UV irradiation.

Hydrogen atom reactions and high irradiation are predictors of **secondary reaction products** for solid hydrocarbons [16]. EPR is also an ideal metric for the analysis of these complex radicals. For example, the H atoms in the frozen aqueous solutions of **H_2SO_4, H_3PO_4,** or **$HClO_4$** present at liquid nitrogen temperatures (77 K) are quite stable. This provides excellent environments for future work [21].

2.2.2. X and gamma ray irradiation

2.2.2.1. Organic compounds

Radiation of an organic material can lead to breakage of bonds between atoms. The minimum energy required for such a situation can be determined by the bond strength [21, 22]. Schneider et al. [23] observed the first electron spin (paramagnetic) resonance spectrum of radicals obtained from the organic polymethylmethacrylate compound by X-irradiation. They produced a very large electron spin (paramagnetic) resonance spectrum giving a complex hyperfine structure splitting. With the detailed analysis of the EPR spectrum, it is understood that the actually occurring state is the result of two separate interaction mechanisms in the $R-CH_2-\dot{C}(CH_3)(COOCH_3)$ radical [24, 25].

Gordy et al. [26, 27] have begun to investigate the radicals of biological substances exposed to X-radiation. As a clear result of the radiation damage, they found that the hyperfine splits originate from simple radical forms. The organic materials that gave these spectra were the various irradiated amino acids. Their EPR spectra were obtained after irradiation with 50 kV X-rays at room temperature. The triplet was obtained from glycine, $CH_2(NH_2)COOH$. The hyperfine interaction ion is due to a $\dot{C}H_2$ radical having two protons. X-rays or other high-energy radiation can break down the molecules and create a variety of radicals. There are many ways to create radicals. One of them is to remove an electron, which is the primary action of irradiation, and to form an ionized molecule with small stable groups such as NH_3CO_2 and $(CH_2)^+$ fragments of glycine [26].

It has been observed that the EPR spectrum of the irradiated alanine, $CH_3.CH(NH_2).COOH$, has five symmetrical lines. This suggests that the unpaired electron interacts with four equivalent protons and that the spin density is in a $(H_2C-CH_2)^+$ group due to hyperconjugation [26].

It has been observed that the EPR spectrum obtained from the irradiated valine, $CH_3.CH(CH_3).CH(NH_2).COOH$, is composed of five and seven overlapping lines. The seven-line splitting was

assumed to originate from a $(H_3C - CH_3)^+$ radical group and was found to be larger than that obtained from UV-irradiated isopropyl alcohol [20]. This may be due to the partial electron withdrawal of the OH group in the structure giving the seven-line splitting.

However, as in the case of UV-irradiated spectra and in stable aromatic ions, the theories of hyperfine interaction and hyperconjugation reveal these spectra in detail. Line widths are the same as those obtained from frozen UV-irradiated glasses. Thus, it can be argued that motional narrowing in these systems is due to dipolar interaction in the nearest proton.

Gordy et al. [26, 27] studied various amino, carboxylic, and hydroxy acids that have been X-irradiated. In some studies, large symmetric doublets are presumably due to the dipole-dipole interaction between the unpaired electron localized on an oxygen or a sulfur atom and a single proton near it. They also investigated the effect of temperature on the carboxylic acid spectra. The irradiated acetic acid is a good example of this. The hydrogen bond keeps the molecules very hard at 77 K. Thus, it has been assumed that the doublet occurs from the dipole-dipole interaction between an electron and a hydroxyl proton localized on hydroxyl oxygen [27].

Gordy et al. [26] obtained spectra obtained from X-radiation of various biological materials such as proteins and bone tissue. Comparing these spectra with those obtained from simpler acids, one can get an idea of the deterioration mechanisms in natural products. Uebersfeld et al. [28–30] studied sugar, cellulose, and similar materials exposed to gamma rays in detail. In their later work, they obtained an anisotropic EPR spectrum from a single crystal of glycine [31]. A similar situation has been observed in the study of single crystals of the X-irradiated alanine by Van Roggen et al. [32]. Whiffen et al. [25, 33] have also done much research on the analysis of EPR spectra from gamma-irradiated polymers with interesting "**oxygen effects.**".

DNA is an organic compound. The EPR spectrum of the radical formed in gamma-irradiated DNA is shown in **Figure 1** [34]. As another organic compound, potassium hydroquinone mono-sulfonate (PHM) may be mentioned. In potassium hydroquinone monosulfonate single crystal, EPR spectrum of the radical structure resulting from gamma irradiation is shown in **Figure 2** [35].
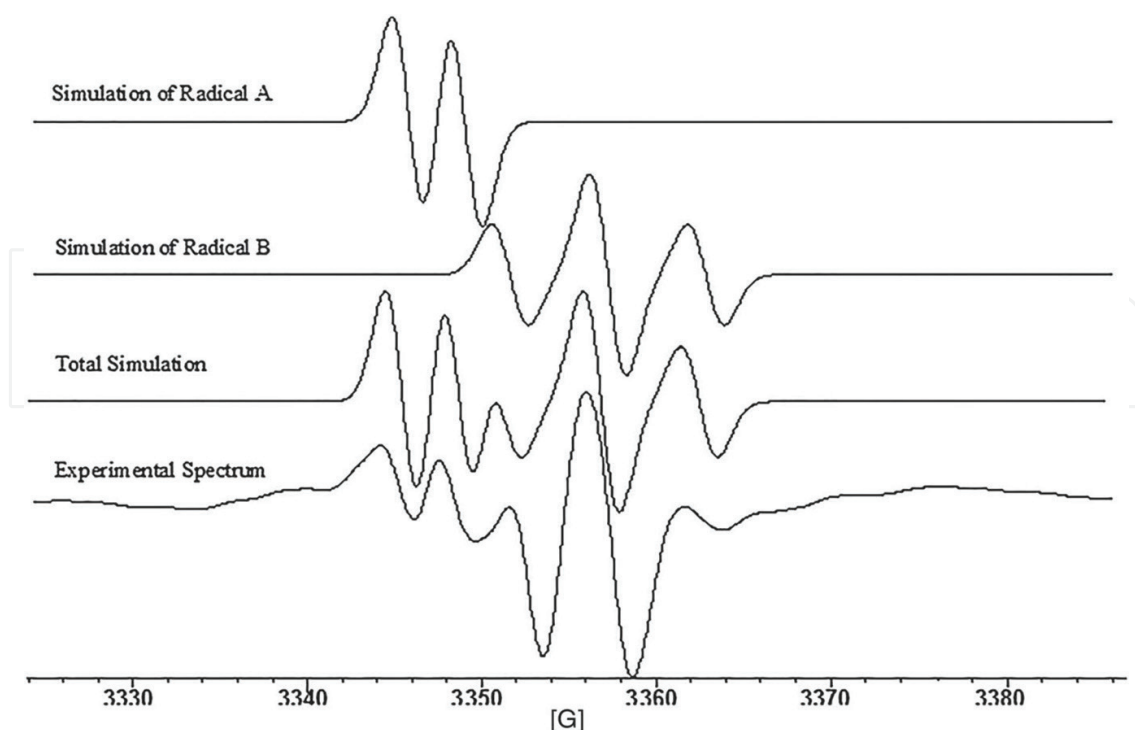
2.2.2.2. Inorganic compounds

Irradiation of **inorganic materials**, usually in a single crystal form, produces centers of damage trapped within the crystal lattice. This can form free atoms, molecules, or radicals in the crystal

Figure 1. The EPR spectrum of the gamma-irradiated DNA at 77 K.

Figure 2. EPR spectrum of gamma-irradiated PHM single crystal at 125 K.

as well as breakage of chemical bonds [21]. The paramagnetic entities produced by the irradiation in these alkali halide crystals can hardly be termed "**free radicals**" in the normal sense of the word. They are better classified as "**damage centers**" or "**defects**" since they are associated with the structure of the crystal itself, rather than a broken bond in a particular molecule.

The EPR study of irradiated inorganic compounds was made before organic samples. Hutchison [36] is the first person to work on this subject. He studied the EPR spectra of lithium fluoride crystals irradiated with neutrons for several hours. This work was followed by X-irradiation studies by researchers such as Schneider and Britain [37], Tinkham and Kip [38], and Kip et al. [39]. In these alkali halide crystals, it is more accurate to denote radiation-generated paramagnetic objects as "**damage centers**" or "**defects**" rather than "**free radicals.**"

Calcite is an inorganic material. The EPR spectrum of the radical structure of gamma-irradiated calcite is shown in **Figure 3** [40].

The damage centers generated by high-energy irradiation in inorganic single crystals can be examined in three categories:

a. *F*-centers,

b. *V*-centers,

c. *U*-centers (Interstitial atoms).

2.2.2.2.1. F-centers

Negative ion deficiency (a halogen vacancy, an anion vacancy) in the lattice and **trapping of an unpaired electron (trapped electron) in the Coulomb field** of the vacancy create **an**
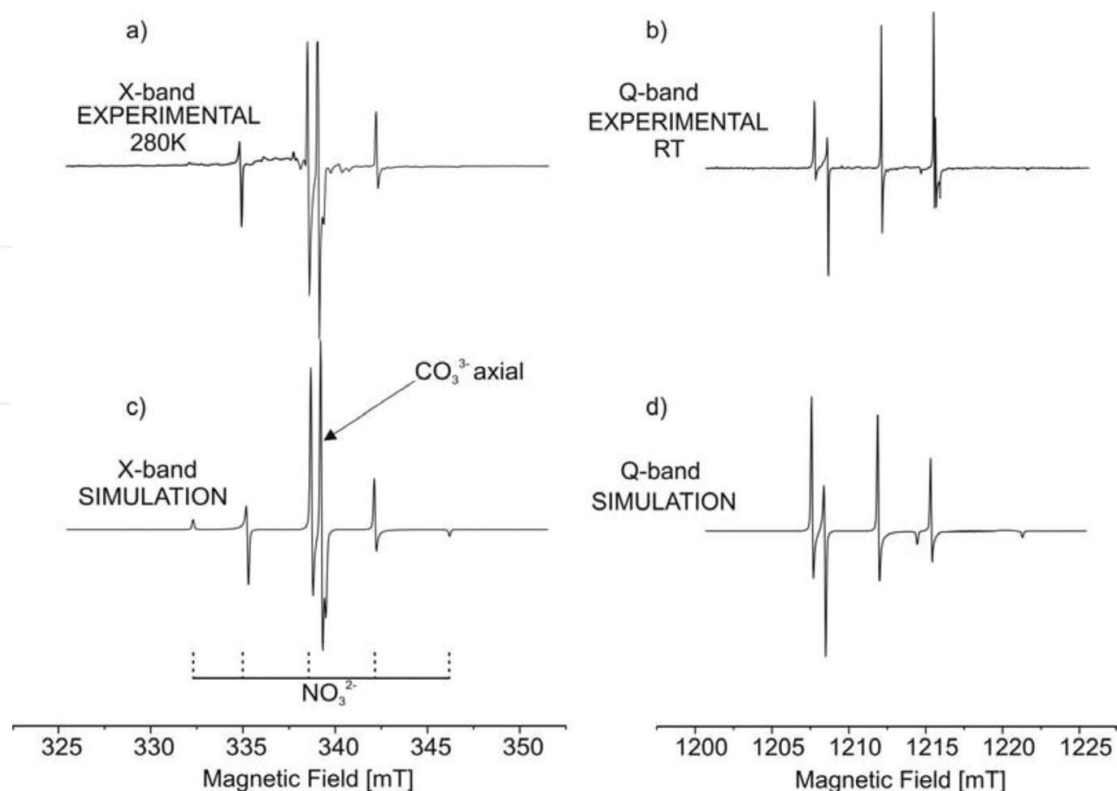
Figure 3. EPR spectra of gamma-irradiated calcite at 77 K recorded at room temperature: (a) X-band spectrum; (b) Q-band spectrum; (c) the simulation of the X-band spectrum; and (d) the simulation of the Q-band spectrum.

F-center. The unpaired electron also moves on neighboring ions. Previous results of F-centers have also been confirmed by Feher's double resonance experiments [41]. Thanks to this technique, all the hyperfine splitting of the F-center in **KCl** can be solved and the coupling constants can be measured in detail. Resolved hyperfine structure has been examined by Lord [42], who studied the F-centers formed in **LiF** and **NaF**. Many authors have studied the molecular orbital interaction theory of the unpaired electron of the F-center [39, 43–50].

EPR spectra of the X-irradiated $LiBaF_3$ crystal along the [100], [111], and [110] directions are given in **Figure 4**. EPR spectra of F-centers formed according to the main orientations of the $LiBaF_3$ crystal were clearly observed [51].

2.2.2.2.2. V-centers

The opposite of **an F-center** is **a V-center**. **A positive ion deficiency (a cation vacancy) in the lattice** and **a deletion of electrons (trapped hole center) in one of the neighboring ions** form **a V-center**. Thus, **this hole**, which is scattered over orbital neighbor ions, is **trapped in vacancy**. When two such **V-centers** are generated side by side, **a V_2-center** is obtained. In this case, the spins of the two electron holes are doubled and the paramagnetism ceases to exist. **A V_3-center** can be defined as **a V_2-center** with only one missing electron or hole between both vacancies. There is an unpaired spin like **a V_1-center**. Kanzig made initial measurements on V-centers [52]. V-centers were obtained by X-irradiation of **KCl** at 90 K. A g-value was found between 2.0023 and 2.024 and was observed to be anisotropic. Anisotropic situation has occurred due to the fact that the hyperfine splitting originating from the two chlorine
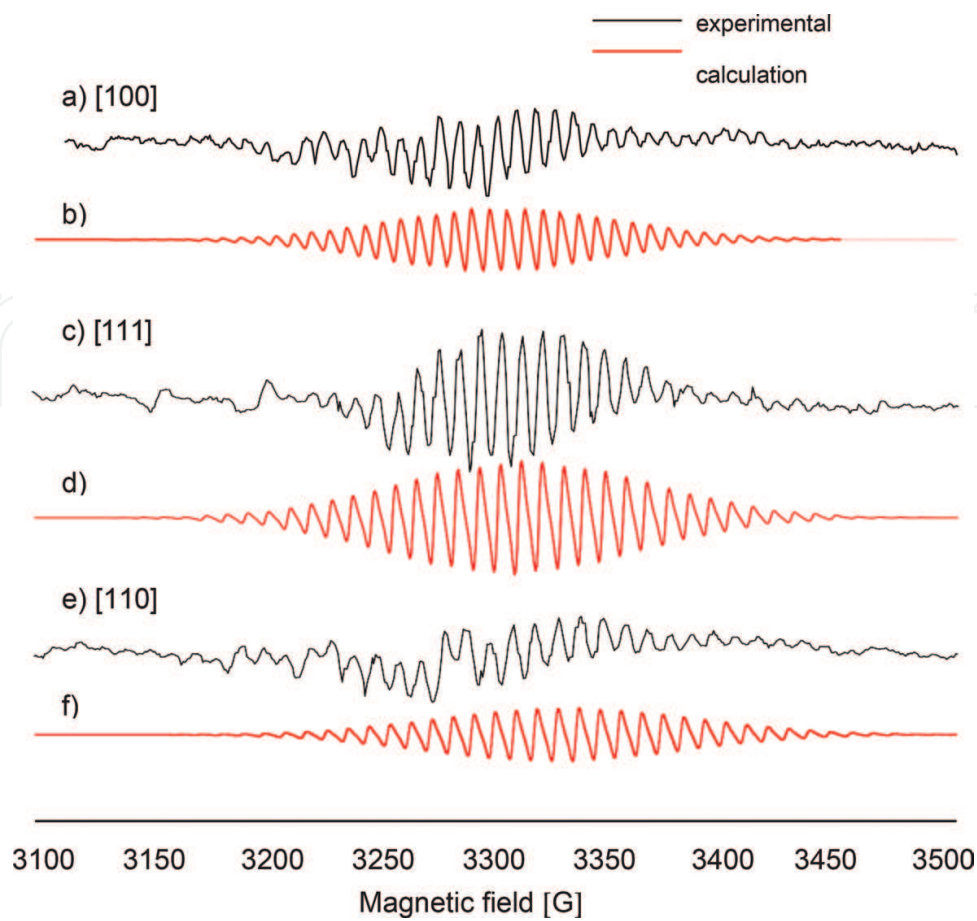
Figure 4. EPR spectra of the F-centers in the LiBaF3 crystal.

nuclei (Cl_2^- ion) shows an angle-dependent change. For this reason, the vacancies are defined as V_3-centers rather than V_1-centers, because V_3-centers must have a central cubic symmetry [53]. The results are consistent with the measurements made on X- and gamma-irradiated and **thallium-activated KCl** [54]. The observed g-value can also be calculated very well by molecular orbital theory [55].

EPR spectra of defects occurring in ZnO with ultraviolet effect are given in **Figure 5**. These defects are the oxygen-vacancy and Zn-vacancy centers [56].
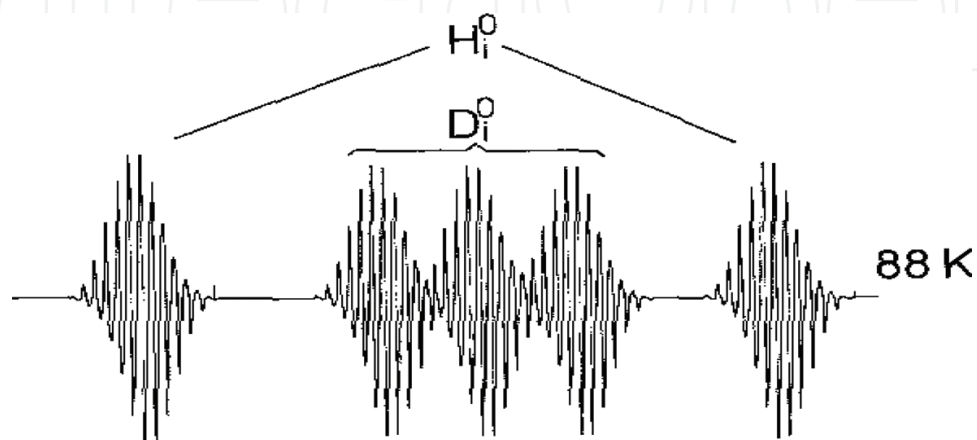
2.2.2.2.3. Interstitial atoms and U-centers

Generally, **interstitial atoms (U-centers)** are obtained when an atom of high-energy radiation, such as neutrons, is sent to an intermediate position from a normal lattice site. For this reason, adding a single atom to the normal ionic bond of the lattice leaves a vacant site. The centers of damage expressed as **F-center** and **V-center** occur in the case of **pure single crystals**. However, if there is **hydride** or **deuteride in the lattice**, it is possible to create **U-centers** defined as **negative ion vacancies containing a hydrogen or a deuterium negative ion**. Thus, the unpaired electron is localized on hydrogen and brings a large doublet hyperfine splitting. The best example of a defect generated by interstitial atoms is **neutron-irradiated diamond**. Griffiths et al. [57] studied the electron spin (paramagnetic) resonance
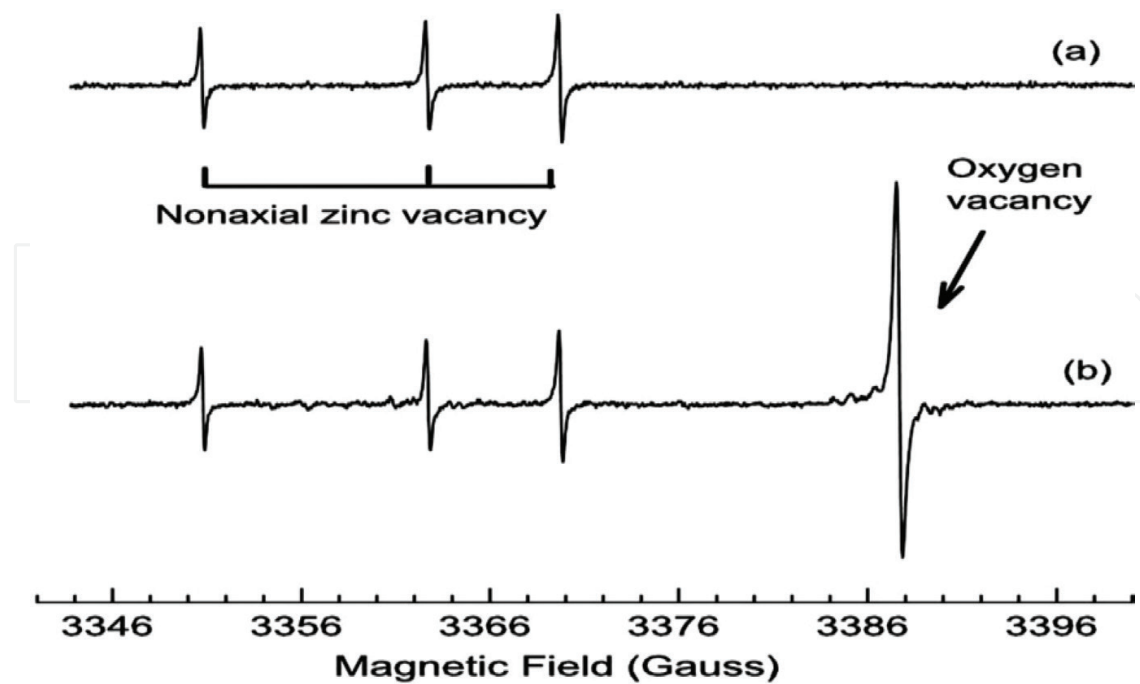
Figure 5. EPR spectra of ZnO **(a)** in the dark and **(b)** after illumination with 325-nm light.

spectrum of this defect and obtained a strong central line with very weak satellites. While
the central line [58] forms single interstitial carbon atoms, the satellites defined by mag-
netic centers also bring about double interstitial aggregates forming C_2 molecules. Wertz
et al. [59] found that the trapping centers were produced at the same time as the interstitial
atoms during their work on **neutron-irradiated magnesium oxide**. In the vacancies created
by neutron irradiation, electrons are trapped and a well-resolved hyperfine structure split-
ting is obtained from neighboring Mg nuclei [41]. Delbecq et al. [54] observed **U-centers** in
irradiated mixed crystals of KCl-KH and **KCl-KD**. In this study, it is seen that the unpaired
electron interacts with the negative ion vacancy and has a doublet of 500 G for **hydrogen**
and a triplet of 78 G for **deuterium**.

Figure 6. The EPR spectrum of $H i 0$ (U_2-center) and $D i 0$-centers into (LiH) +.

At low temperatures below 70 K, interstitial atoms are produced by ultraviolet or X-ray irradiation. These atoms form in hydrogenated or hydroxyl-doped crystals. In the KCl, the H_i^0-center (U_2-center) and D_i^0-center are observed due to the ultraviolet effect [60]. In KCl, the $(LiH)^+$-center is transformed to produce H_i^0-center (U_2-center) and D_i^0-center. The EPR spectrum of the resulting H_i^0-center (U_2-center) and D_i^0-center is shown in **Figure 6**.

3. Conclusion

In addition to chemical reaction and thermolysis methods, a material is subjected to a series of changes by irradiation. Photolysis or radiolysis processes are used as irradiation methods. However, radiolysis is more effective. Radiolysis is a process performed using ionizing radiation. Ionized radiation is separated into charged and uncharged particles. In this group, X-rays and gamma rays are used more effectively than neutrons. Interactions of such high-energy noncharged particle radiation or indirectly ionizing radiation with matter are effective in breaking chemical bonds or ionizing the structure. Breaking of the structure and its ionic conversion are expressed as free radicals and ionic radicals, respectively.

When organic and inorganic substances are exposed to ionizing radiation, the bond structures deteriorate. In organic and inorganic materials, UV, X-, or gamma rays can give rise to ionic radicals or free radicals. The radiation damage centers in inorganic materials can be seen as *F*-center, *V*-center, and *U*-center. In inorganic pure single crystals, *F*- and *V*-centers are named as radiation damage centers, negative ion deficiency, and positive ion deficiency, respectively. As the radical lifetimes can be very short, the detection of the radical becomes difficult. To overcome such a difficulty, EPR analysis is often performed at low temperature. The life of the radical in the sample, which is kept at low temperature, is extended.

In EPR studies, irradiation of organic or inorganic material is the first step. The type of radiation used must be highly energized. Using gamma rays leads to more accurate results. The second step is to perform EPR analysis at low temperature (77 K). Thus, the single electron formed by breaking the bonds is provided to be trapped at the point where it exists. At low temperature, the removal of the radical from the environment and the damping of the radical are prevented. This provides the appropriate time for the analysis of the radical.

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