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Photonic irradiation induces nano-structures – an EPR study

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During the irradiation of fluorite (CaF_2) with photons (X) we observe the formation of nano ordered structures (inclusions). This forming structure is homothetic in relation to the fluorine ions of the crystal. The particles of approximately 10 nm size agglomerate and form *nanostructures structures with parallelipipedic shape*. The length of these structures varies between 30 and 3000 nm. The local changes of symmetry produced by the formation of the nano structures can be inferred from EPR measurements on *Kramers rare earth ions* introduced in CaF_2.

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1. Introduction

A very large number of papers were devoted to the study of the changes induced in the irradiated crystals. Among the most significant, in our opinion, are the papers [1-4]. In these papers it is evidenced the role of the point defects (essentially, *F centers*) in the changes appearing as the result of the irradiation with high-energy X photons (more than 1 keV).

It seems that the F centers are produced according to the following scenario [5,6]: the incident photons ionize mainly the anionic sites. The anion ionization produces at the site a positive charge (a hole or an anionic vacancy). The vacancy traps an electron, which compensates its positive charge. The electron and the vacancy constitute a hydrogen-type object with characteristic energy levels. The resulting selective absorption is responsible for the color of the crystal (normally transparent). The assembly anionic vacancy + electron is named F center (from the German word "Farbe" for color).

To simplify, the F center can be considered as a cubic box containing an electron. The eigenvalues of the electronic energy are (if the potential vanishes inside the box and is infinite outside): $\frac{\hbar^2}{2m_0}\frac{\pi^2}{a^2}\left(n_x^2+n_y^2+n_z^2\right)$, where $\hbar$ is the rationalized Planck constant, m_0 is the electron mass and n_x, n_y, n_z are non-null integer numbers. In the ground state $n_x = n_y = n_z = 1$, i. e. the ground state is not degenerated. The first excited state is three times degenerated: (2,1,1), (1,2,1), (1,1,2). The irradiation with photons could distort the site, and that is equivalent with a *local symmetry change*. This distortion reduces the symmetry of the F center, removing partially the degeneracy, and diminishes the energy of the defect. The energy-configuration diagram [5] shows that the state (1,1,2) – representing an elongation or a contraction of the lattice around the F center – is predisposed to such a distortion. This spontaneous distortion of the F center (observed, also, for other defects or crystals) is of the Jahn-Teller type. Due to this effect the energy of the state is lowered, the energy being shared with two anionic neighbors, resulting an X_2^- (Fluorine, in this case) molecule oriented along <110> direction.

This molecule, very electrophile, traps an electron which forms with the hole another hydrogen-like state, named *exciton*. This state is shared by two neighboring anions. The local distortion (for instance, a contraction) stabilizes this excited state denoted (1,1,2). The radiative energy of the de-excitation, diminished by the lattice distortion, could take the value zero (if the configuration-distortion curves intersect each other). In this case the energy of this non-radiative transition is completely transferred to ions. Taking into account the symmetry, the most probable event is the ejection of one of the two ions A^- in the direction of the molecule X_2^-. This direction is "dense" and formed by A^- ions of the same mass. At the time of a non-radiative de-excitation, an anion returns to its site while the other one, leaving the site, send off the nearest neighbor. The origin of this process is the photon impact; successive impacts propagate with low losses. For enough initial energy (5-8 eV), the initial ion drives off its neighbor, this one drives off its neighbor and so on. Finally,

after this series of collisions, a vacancy A^- remains in the initial position while an interstitial is present at some atomic distances where two anions share the same site. The energy of the non-radiative transition can be either found as the energy to create the two defects (vacancy '*v*' and the interstitial '*i*') or dissipated by the thermal agitation during collisions.

As a conclusion, we must emphasize that the creation mechanism of the nano-structures by irradiation is not yet elucidated. In order to understand better this mechanism, a series of EPR experiments on irradiated samples doped with *Kramers rare earth ions* (Er^{3+} and Sm^{3+}), has been carried out.

2. Experimental

The CaF_2 single crystals, doped with Er^{3+} and Sm^{3+} have been grown in the Solid State Quantum Electronics Laboratory - National Institute for Lasers, Plasma, and Radiation Physics. Er^{3+} and Sm^{3+} substitute Ca^{2+} in the CaF_2 lattice. Samarium enters, also, as Sm^{2+}, with non-vanishing Van Vleck susceptibility (χvv). This susceptibility influences the positions and the intensities of the EPR signal of Sm^{3+}. Erbium enters only as Er^{3+}.

The CaF_2 single crystals were grown in argon atmosphere. Prior to the growth, the CaF_2 was purified by thermal treatments and zone melting. The doping concentrations were 1.5 % mol for Sm and 0.1 % mol for Er. Samarium was introduced as a metal while Erbium was introduced as Er_2O_3. The initial concentrations (in the non-irradiated samples) of Sm^{3+} and Er^{3+} were the same (0.05 at. % relative to Ca^{2+}). Therefore, the intensity of Sm^{3+} EPR signal had the same order of magnitude as the Er^{3+} signal.

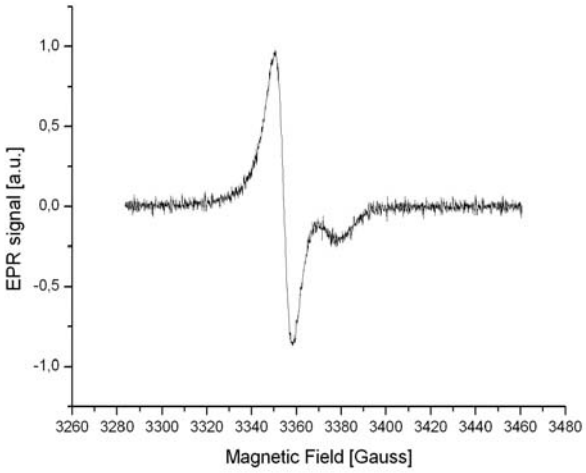
For crystalline structures of the fluorite type the EPR studies evidenced the role of the symmetry of the ligand field in the process of the energy transfer between the electronic energy levels. By irradiating such a crystalline structure with X-rays (~50 keV) we observe that the symmetry change of the ligand field induces the anisotropy of the $\hat{G}$ *tensor* (tensor of spectral decomposition).

In a crystalline structure of fluorine type when the RE^{3+} (RE = rare earth) ion enters a site with cubic symmetry substituting a divalent metal ion Me^{2+}, the EPR spectra of RE^{3+} are rather complex. For Sm^{3+} it is difficult to interpret the EPR spectra in the frame of the first order of perturbation due to the small gap (~1000 cm^{-1}) between the first excited state and the ground state $^6H_{5/2}$. In contrast, the components $g_{\|}$ and $g_{\perp}$ of the $\hat{G}$ tensor are well identified. In this case the gap between the first excited state $^4I_{3/2}$ and the ground state $^4I_{15/2}$ is large enough (~6000 cm^{-1}) and thus the first order theory of perturbations is correct.

Due to the charge compensation, the site symmetry, initially cubic, changes into longitudinal tetragonal and/or into diagonal trigonal symmetry. Nevertheless, some sites remain cubic. The new result reported in this paper is the presence of an intense EPR signal characterized by a $\hat{G}$ tensor with trigonal symmetry. This signal is very intense in the irradiated sample but it is present, with lower intensity, in non-irradiated sample.

2.1. EPR measurements on irradiated sample

The non-doped fluorine sample does not give any EPR signal. After the irradiation with 50 keV X photons (4 hours and, respectively, 8 hours) the EPR signals with $g \approx 2$ are clearly observed. These EPR signals (Figs. 1 and 2) were recorded for a fixed frequency (9.4 GHz) and a variable magnetic field (3200 ÷3400 Gauss).



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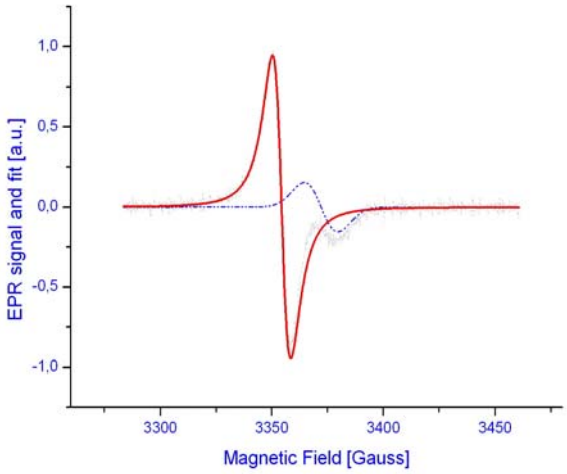

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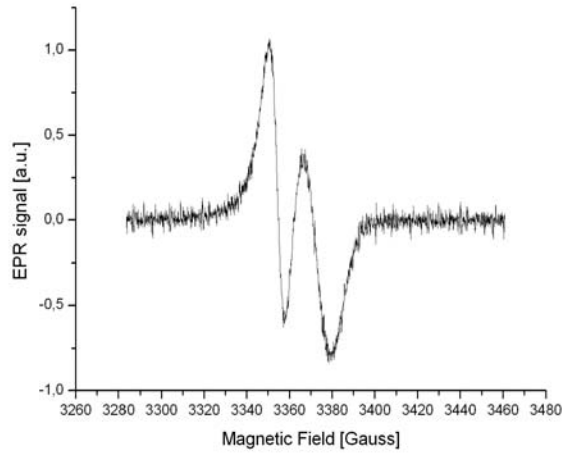
Fig. 1.a The EPR signal recorded on a CaF_2 sample irradiated for 4 hours with 50 KeV X-ray photons. b The Poincaré's fit evidences the complex structure of the line: - a dominant Lorentzian contribution (~85%) due to the F centers (thick, solid line); - a minor Gaussian contribution (~15%) due to the conduction electrons (thin, dotted line).



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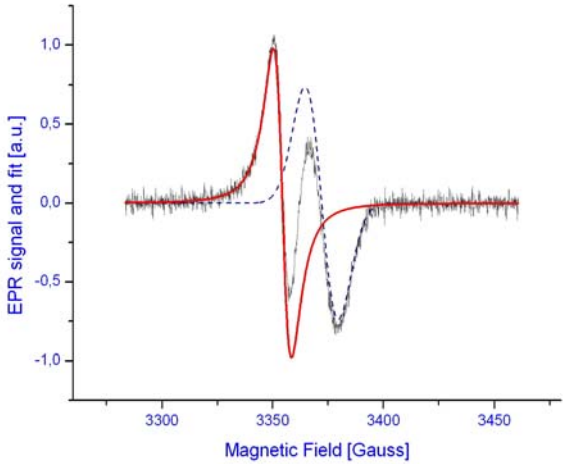

b

Fig. 2.a The EPR signal recorded on a CaF_2 sample irradiated for 8 hours with 50 KeV X-ray photons. b The relative contributions of Lorentzian (F centers - thick, solid line) and of Gaussian (conduction electrons - thin, dotted line) lines changes from 85 % : 15 % to 55 % : 45 %.

Using the Poincaré fit method [8] we put in evidence the complexity of the EPR signal: a Lorentzian line (due to F centers) and Gaussian line (due to the conduction electrons) are superimposed. The measurements evidenced the increase of signal of the conduction electrons as one goes along the formation of the metal nano-structures in the crystalline structure of CaF_2. The CaF_2 structure is initially insulating and without any magnetization. Once irradiated, the presence of EPR signal typical for F centers [1] supports our hypothesis concerning the role played by this type of defects in the formation of the nanometer metal inclusions. The experiments on doped samples allowed to refine our models.

2.2 Samarium-doped sample

In CaF_2 the samarium ion (divalent or trivalent) substitutes the divalent cation Ca^{2+}. Sm^{2+} is not paramagnetic but posses a Van Vleck susceptibility. This susceptibility could produce, in certain neighborhood conditions, a shift of the EPR signal of Sm^{3+} centers.

2.2.1 Experiments on non-irradiated samples

The EPR spectra were recorded at 4 K for a fixed frequency (9.46 GHz) with a magnetic field varying between 7000 and 13000 Gauss. Our measurements show the presence of centers corresponding to two types of symmetry: ones with cubic and others with lower symmetry (C_{4v}). In the last case the $\tilde{G}$ tensor corresponds to the axial symmetry of the axes [100], [010] or [001]. We obtained $g_{\|} = 0.90\pm0.01$ and $g_{\perp} = 0.77\pm0.01$. The average value is $\tilde{g} \approx 0.837$ along the direction <100>. This value is higher than value for the isotropic g, corresponding to the cubic symmetry for Γ_7 ($g \approx 0.467$). This proves the existence of a magnetic exchange between Sm^{3+} and Sm^{2+}. The exchange provokes, also, a Δg shift.

The Sm^{3+} spectrum contains, for an arbitrary angle, three lines (Fig. 3).

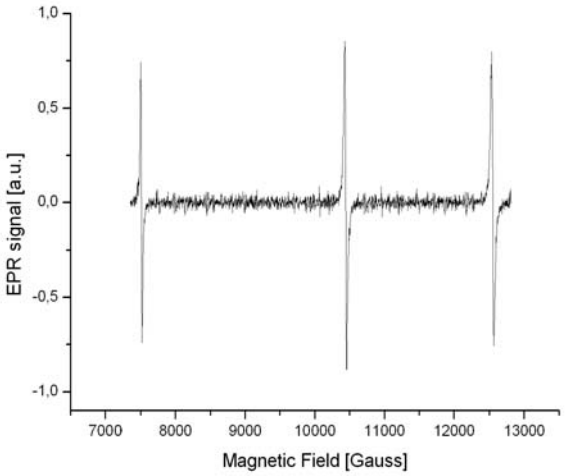

Fig. 3. EPR signal of Sm^{3+}: CaF_2 irradiated 8 hours with 50 keV X photons.

For various orientations the values of g show an angular anisotropy. For an axial symmetry of the crystal field type <100> there are, for an angle θ, three classes of resonators, according to the three possibilities: [100], [010] and [001]. If θ is the angle between [100] direction and the magnetic field $\vec{H}_0$, the angle θ takes the values $\theta, \frac{\pi}{2} - \theta$ and $\frac{\pi}{2}$ for the resonators x, y, z.

2.2.2 Experiments on irradiated samples

The irradiation with 50 keV X-rays leads to the formation of point defects. These defects favor a supplementary valence change $Sm^{2+} \rightarrow Sm^{3+}$. This change is produced by an extrinsic mechanism due to interstitial de-location of Sm or by the vicinity of a defect in the ligand lattice. The last possibility seems to be more probable, the formation of fluorine vacancies being the most probable process at this irradiation level. As a result of the irradiation, a global increases of ~ 10% of the EPR signal due to the increase of the number of resonant centers. On the other hand, the line positions are shifted, as a result of the new numerical presence of the Sm^{2+} ions. The last effect is provoked by the modification (via the number *p* of the Sm^{2+} nearest neighbors) of the Van Vleck susceptibility. This suggests that approximately 10% Sm^{2+} ions became Sm^{3+}.

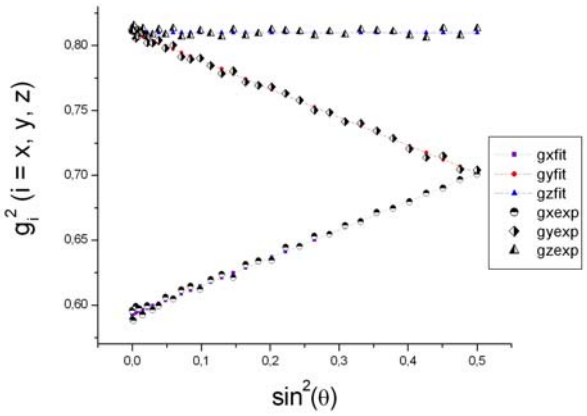

Fig. 4. Diagram $\left[g^2; \sin^2\theta\right]$ *for* Sm^{3+}*:* CaF_2 *irradiated 8 hours with 50 keV X photons.*

In this case, the charge compensation plays a determinant role when the symmetry of the ligand field changes. The analysis of the EPR signals of Sm^{3+}, modified by the symmetry change of the sites, is a very difficult task. As we already mentioned, the gap between the ground sate $^6H_{5/2}$ and the first excited state $^6H_{7/2}$ is rather small (~1000 cm^{-1}). It is easier to interpret these symmetry changes for the EPR signals of Er^{3+} ions: the energy gap separating the ground state $^4I_{15/2}$ and the first excited state $^4I_{13/2}$ is much larger (~6000 cm^{-1}).

2.3. Erbium-doped sample

The trivalent Er^{3+} ions enter the cubic structure of CaF_2 by a heterovalent substitution of Ca^{2+}. The charge compensation induces the formation of a defect which modifies the site symmetry. Three types of symmetry are evidenced: cubic, tetragonal and / or trigonal. In tetragonal symmetry there are three equivalent sites along the [100], [010] and [001] crystal axes. The proposed notations for [100], [010] and [001] crystal axes are: T_X, T_Y and T_Z. The four *trigonal axes* correspond to the directions $[111]$, $[\bar{1}\,11]$, $[\bar{1}\,\bar{1}\,1]$ and $[1\,\bar{1}\,1]$.

2.3.1 Experiments on non-irradiated samples

The EPR spectra were recorded at 4 K and 9.46 GHz. The magnetic field varies around 1000 Gauss. The diagram $\left[g^2/\sin^2\theta\right]$ gives the components of the $\hat{G}$ tensor. The results are given in Table 1.

Table 1. Components of the $\hat{G}$ *tensor in non-irradiated* Er^{3+}*:* CaF_2*.*

Components of the $\hat{G}$ tensor → Symmetry ↓	$g_{\|}$	$g_{\perp}$
Cubic	6.80	6.80
Tetragonal	7.80	6.25
Trigonal	3.30	8.55

The obtained values are close to the values reported by Ranon and Low [7] for the *tetragonal spectrum* of the type I, i. e. $g_{\|} = 7.78$ and $g_{\perp} = 8.54$ (Fig. 5), but we found very different intensities, corresponding to the same angular values of the magnetic field relative to the T_Z axis. For the non-irradiated sample we found that the

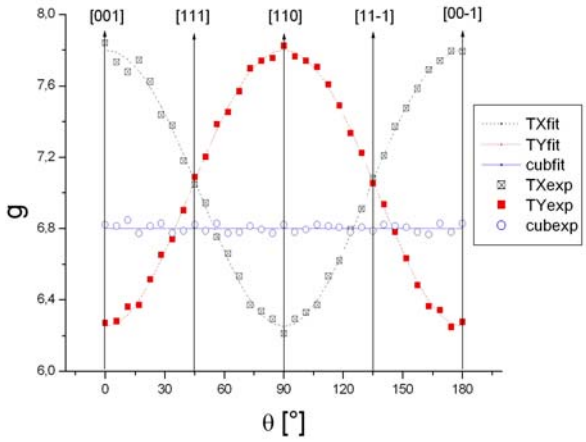

Fig. 5. Angular dependence of the components of the $\hat{G}$ *tensor in non-irradiated* Er^{3+}*:* CaF_2*;* θ *is the angle between [100] direction and the magnetic field* $\vec{H}_0$*.*

intensities of the signals are in the following ratios: T (tetragonal) : t (trigonal) : c (cubic) = 4 : 2 : 3. No tetragonal or trigonal signal of the type II (cited in [7]) was detected in our spectra.

2.3.2 Experiments on irradiated samples

For the irradiated samples the lines have the angular evolution given I Fig. 6. The angular diagrams were constructed from the EPR spectra whose parameters were identified using the Poincaré's treatment [8].

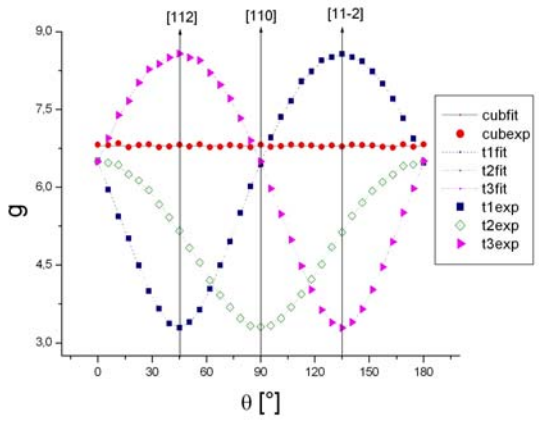

Fig. 6. Angular dependence of the components of the $\widehat{G}$ tensor in Er^{3+}: CaF_2 irradiated 8 hours with 50 keV X photons.

In this case, the intensity ratio is T : t : c = 8 : 5 : 4. We must emphasize that our crystals were grown in neutral atmosphere. The significant increases of the trigonal signal in the irradiated samples are probably due to the presence of oxygen. We suppose that the absence of the trigonal spectra of type II (whose intensity increase is reported in [7]) is related to compensation with oxygen placed diagonally in a fluorine position. This oxygen came from the Er_2O_3 doping.

3. Conclusion

The comparison of Er^{3+} EPR spectra in irradiated and in non-irradiated CaF_2 samples led us to the following conclusions:

- the lines conserve their angular dependence;
- the intensity of the cubic lines decreases;
- the intensity of the tetragonal lines increases slightly;
- the intensity of the trigonal lines shows a significant increase;
- the total number of resonant Er^{3+} centers is rigorously the same in both irradiated and non-irradiated samples.

We put in evidence a symmetry change of the ligands F^- from cubic toward C_{4V}. The tetragonal change is explained as a result of charge compensation with an interstitial defect created by an F- ion occupying the center of the neighbor ligands, initially empty. In the trigonal case we suggest that an O^{2-} ion replaces a F^- ion in a cube corner of neighboring fluorine ions.

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