

Dedicated to Professor Valentin I. Vlad's 70th Anniversary

HIGH THERMAL STABILITY OF THE OFF-CENTER PARAMAGNETIC Fe^{3+} IONS IN CHLORINATED $\text{SrCl}_2:\text{Fe}^{2+}$ CRYSTALS

D. GHICA and S.V. NISTOR*

National Institute of Materials Physics, P.O. Box MG-7, RO-077125 Bucharest-Magurele, Romania
*E-mail: snistor@infim.ro

Received June 17, 2013

Abstract. The thermal stability above 300 K of the hole-trapped Fe^{3+} centers, formed by X-ray irradiation at 80 K in chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystals, has been investigated by Electron Paramagnetic Resonance. In the temperature range of 300 - 520 K, the trigonal Fe^{3+} center completely transforms into the cubic Fe^{3+} center, which further decays up to 700 K. The formation and transformation of the trigonal Fe^{3+} center, containing off-center Fe^{3+} ions, is associated with the presence and thermally activated movement of the interstitial Cl^- ions, present in excess in chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystals.

Key words: SrCl_2 , Fe-related paramagnetic centers, electron paramagnetic resonance.

1. INTRODUCTION

Designing new materials/molecular magnets with large magnetic anisotropy energies (MAE) for applications in information storage and quantum computing is highly demanded. Transition metal ions (TMIs) with electron spin $S > 1/2$ in the ground state, with a large off-center displacement in a cubic lattice are of interest due to the recently reported [1,2] high magnetic anisotropy of Fe^+ ions in KTaO_3 and SrCl_2 . In the case of the Fe^+ ions in $\text{SrCl}_2:\text{Fe}^{2+}$, a MAE of 106 cm^{-1} was calculated [2], higher than the *giant* value of 72 cm^{-1} reported for a Co atom placed on a (111) Pt surface [3].

For isolated $3d$ ions with $S > 1/2$, $\text{MAE} = 2|D|$, where D represents the zero-field-splitting (ZFS) parameter of the corresponding interaction in the spin Hamiltonian [4]. Typical values of $|D|$ for Kramers ions in inorganic insulators are in the range of $0.01 - 1 \text{ cm}^{-1}$ [4]. Therefore a detailed microstructural study of the Fe^+ and Fe^{3+} based paramagnetic centers and their thermal stability in $\text{SrCl}_2:\text{Fe}^{2+}$ is important for understanding its special magnetic properties. Electron Paramagnetic

Resonance (EPR) and Electron-Nuclear Double Resonance (ENDOR) are methods of choice when investigating the microstructure of the paramagnetic TMIs in insulated and semiconducting materials [4, 5].

Iron enters the fluorite cubic-lattice of SrCl_2 as Fe^{2+} ($3d^6$). Thus it is expected that the electrons and holes resulted by irradiation with ionizing radiation to be trapped at the Fe^{2+} ions and to produce both Fe^+ ($3d^7$) and Fe^{3+} ($3d^5$) paramagnetic centers with cubic symmetry. When such crystals are grown in an inert atmosphere (pure argon), only the cubic Fe^{3+} centers ($\text{Fe}^{3+}_{\text{cub}}$) are produced by X-ray irradiation [6]. In $\text{SrCl}_2:\text{Fe}^{2+}$ crystals grown in a chlorine atmosphere, i.e. chlorinated, the Fe^{2+} ions are able to trap both electrons and holes produced by X-ray irradiation. In the case of irradiation at low temperature ($T \sim 80$ K), besides the cubic Fe^{3+} center, several primary Fe^+ and Fe^{3+} paramagnetic centers with non-cubic symmetry have been identified and analyzed by EPR and ENDOR: the tetragonal $\text{Fe}^+(\text{I})$ and $\text{Fe}^+(\text{II})$ centers [7-9], the monoclinic $\text{Fe}^+(\text{IIa})$ center [10] and the trigonal Fe^{3+} center ($\text{Fe}^{3+}_{\text{trig}}$) [11]. In the case of the $\text{Fe}^+(\text{II})$ center, the Fe^+ ion was found to undergo a large off-center intrinsic displacement along the tetragonal [001] axis [7,9], producing the giant MAE calculated in Refs. 1,2. Also, in the case of the trigonal Fe^{3+} center, the Fe^{3+} ion is off-center displaced along a trigonal $\langle 111 \rangle$ axis [11]. Such off-center ions are of particular interest and further investigations of their thermal stability could better explain their unusual non-cubic symmetry and are important for future applications.

Pulse annealing experiments at temperatures up to room temperature (RT), on such low-temperature irradiated chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystals, have revealed the transformation of the $\text{Fe}^+(\text{II})$ -type centers in other two secondary monoclinic centers, $\text{Fe}^+(\text{III})$ and $\text{Fe}^+(\text{IIIa})$, containing also off-center Fe^+ ions [12]. The $\text{Fe}^+(\text{III})$, $\text{Fe}^+(\text{I})$ and both hole-trapped Fe^{3+} centers were found to be stable at RT [7,11,12]. Further pulse annealing experiments at temperatures up to 700 K have been performed and the exceptional thermal stability of the electron-trapped Fe^+ centers has been investigated by EPR [13]. It was shown that above 450 K the $\text{Fe}^+(\text{III})$ center transforms into the $\text{Fe}^+(\text{IV})$ center, with the Fe^+ ion also off-centered. In this work the hole-trapped Fe^{3+} centers are investigated in terms of thermal stability above RT, in order to complete the study of the non-cubic, off-center paramagnetic Fe^+ and Fe^{3+} ions in chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystals.

2. EXPERIMENT

In this work we have used the same Fe (0.1 % mol) doped SrCl_2 single crystals grown by Bridgman technique in a chlorine atmosphere, employed in the previous studies [7-13]. The samples for EPR measurements were cleaved with the long edge along a crystal $\langle 110 \rangle$ direction, with typical size of $3 \times 3 \times 10$ mm³. Before irradiation, the sample was annealed at 700 K for 10 min and quenched at RT in order to disperse the possible iron agglomerates. The X-ray irradiation (W anode at 50 mA and 50 kV) was performed in liquid nitrogen ($T = 78$ K) for 30

min. After irradiation the sample was warmed up at RT, inserted in the microwave cavity and oriented with the magnetic field parallel to an $\langle 110 \rangle$ axis, within 0.5 degrees accuracy, using the low-field EPR transitions of the $\text{Fe}^+(\text{I})$ center. X-band (9.5 GHz) EPR measurements were performed with a Bruker ELEXSYS-E580 spectrometer equipped with a gas-flow cryogenic system allowing operation in the 3.8 to 300 K temperature range, from the Center for advanced ESR/EPR techniques (CetRESav – <http://cetresav.infim.ro/>). The optimum measuring temperature of the EPR lines of all paramagnetic centers was found to be 6–7 K. The successive pulse annealing of the sample at increased temperatures above RT were performed in a temperature stabilized furnace ($\pm 1^\circ \text{C}$) for 5 min, followed by cooling to RT and to the EPR measuring temperature ($T = 6.5 \text{ K}$).

3. RESULTS AND DISCUSSIONS

The EPR line intensity of a paramagnetic center is proportional with its concentration. Therefore, temperature induced transformations at $T > \text{RT}$ of the paramagnetic Fe^+ and Fe^{3+} based centers which are stable at RT could be observed in the corresponding EPR spectra. Figure 1 presents a selection of the EPR spectra recorded at the mentioned annealing temperatures in the low (Fig. 1a) and central ($g \sim 2$) (Fig. 1b) magnetic field regions at microwave powers where saturation of the lines could be avoided. In the low-field region, the EPR lines of the electron-trapped Fe^+ centers and of the hole-trapped $\text{Fe}^{3+}_{\text{trig}}$ center are observed (Fig. 1a). In the central magnetic field region (Fig. 1b), the characteristic EPR spectrum of the $\text{Fe}^{3+}_{\text{cub}}$ center exhibits a resolved super-hyperfine structure of the central fine-structure $\Delta M_S = -1/2 \rightarrow 1/2$ transition, due to the interaction with the first shell of Cl^- ligands.

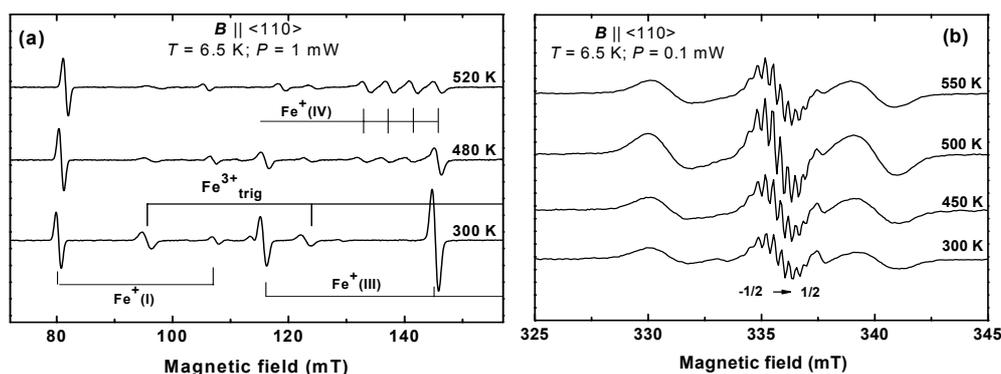


Fig. 1 – Selected X-band EPR spectra, recorded at $T = 6.5 \text{ K}$, of the chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystal X-ray irradiated at 80 K and pulse-annealed at the indicated temperatures: a) in the low magnetic field region; b) in the central ($g \sim 2$) region where the characteristic EPR spectrum of the cubic Fe^{3+} center is visible. Only the central fine-structure $\Delta M_S = -1/2 \rightarrow 1/2$ transition is labeled, for simplicity.

The complete evolution of the EPR line intensity/concentration of the hole-trapped Fe^{3+} centers *versus* the annealing temperature, as determined in the present investigation, is presented in Fig. 2. One finds that the EPR line intensity of the $\text{Fe}^{3+}_{\text{trig}}$ center decreases, while the EPR line intensity of the $\text{Fe}^{3+}_{\text{cub}}$ center increases up to 500–520 K. The transformation of the trigonal Fe^{3+} center into the cubic Fe^{3+} center begins above 300 K and is complete at $T > 525$ K. At higher temperatures, the decay of the cubic Fe^{3+} center is also observed, being complete at 700 K.

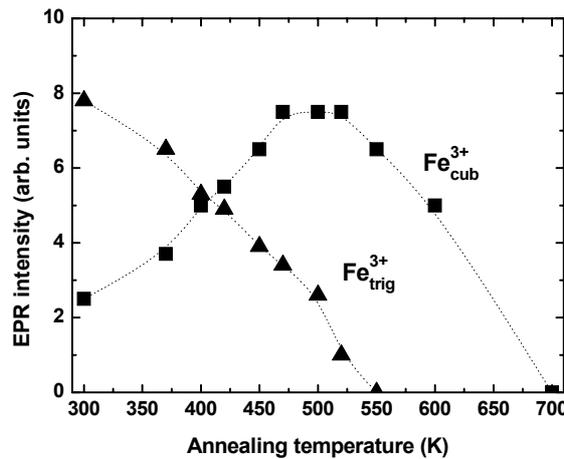


Fig. 2 – Thermally induced transformation of the $\text{Fe}^{3+}_{\text{trig}}$ center into the $\text{Fe}^{3+}_{\text{cub}}$ center in the chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ X-ray irradiated at 80 K and pulse-annealed at the indicated temperatures. The EPR measuring temperature is $T = 6.5$ K. The dotted lines are guides for the eye.

In order to understand the thermally induced changes in the EPR spectra and the associated concentration variation of the paramagnetic centers, we will refer to the structural models of the two hole-trapped Fe^{3+} centers. Their EPR spectra are described by the spin Hamiltonian [4]: $\hat{H}_S = \mu_B \cdot \vec{B} \cdot \vec{g} \cdot \hat{S} + CF$, where the first term represents the electron Zeeman interaction of the $S = 5/2$ electron spin with the magnetic field and the second term describes the interaction of the electron spin with the local crystal field (CF), characterized by the zero-field-splitting (ZFS) parameters B_n^m . The EPR spectra parameters of the two centers are listed in Table 1.

Table 1

Spin Hamiltonian parameters of the hole-trapped Fe^{3+} centers in chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystals. (the ZFS parameters B_n^m are given in 10^{-4} cm^{-1} units)

Center	S_{eff}	g	B_2^0	B_4^0	B_4^{-3}	B_4^3	B_4^4	Ref.
$\text{Fe}^{3+}_{\text{cub}}$	5/2	2.0143	-	0.59	-	-	2.96	6
$\text{Fe}^{3+}_{\text{trig}}$	5/2	2.0141	800.6	-0.44	-10.5	0.33		11

The fluorite structure of the SrCl_2 crystal consists of anionic cubes containing in their center a Sr^{2+} ion, which alternate with empty anionic cubes (Fig. 3a) [14]. Such structure allows the incorporation of a rather large concentration of impurity ions in interstitial positions [14]. The cubic Fe^{3+} center consists in a substitutional Fe^{3+} ion localized in the center of the cube formed by eight Cl^- ions, with a remote defect having a compensating negative charge. In the case of the trigonal Fe^{3+} center, the symmetry lowering from cubic to axial was attributed [11] to the presence of an extra-charged X^{2-} defect along an $\langle 111 \rangle$ axis, replacing one of the eight nearest-neighbor Cl^- ion. Such a defect would explain the electrical neutrality of the $\text{Fe}^{3+}_{\text{trig}}$ center and therefore its thermal stability at RT. Moreover, the large value of the *ZFS* parameter B^0_2 was explained by the Coulombian interaction between the extra-negative charge of the X^{2-} defect and the extra-positive charge of the Fe^{3+} ion, which produced the off-center displacement of the Fe^{3+} ion along an $\langle 111 \rangle$ axis. The most probable candidate for the X^{2-} defect was proposed to be a split di-interstitial $\text{Cl}^- - \text{Cl}^-$ pair, replacing one Cl^- ion, with its axis along an $\langle 111 \rangle$ axis, in order to preserve the axial symmetry of the defect. This model seems highly probable considering the crystal growth conditions in a chlorine atmosphere resulting in the presence of a chlorine excess in the SrCl_2 lattice, expected mainly in interstitial sites. Therefore, such a trigonal Fe^{3+} center as presented in Fig. 3b could be easily formed. Although the presence of an O^{2-} ion replacing one of the nearest-neighbor Cl^- ion was not neglected in discussing the nature of the X^{2-} defect [11], such a structure seems very unlikely considering the gettering property of nascent atomic chlorine present in the crystal growth process *versus* the oxygen.

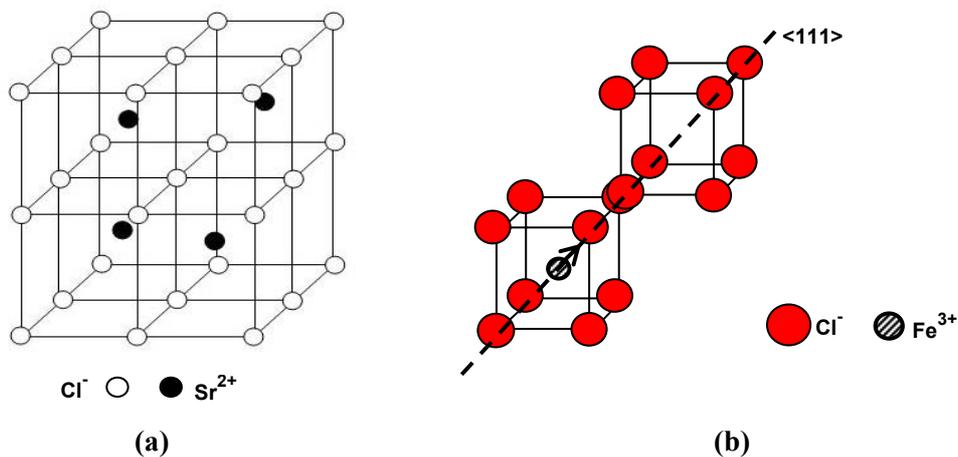
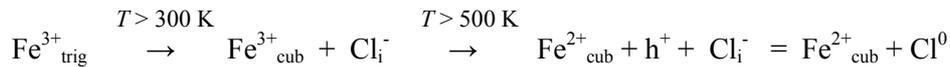


Fig. 3 – a) The fluorite-type structure of the SrCl_2 crystal consisting in the alternant presence of empty anionic cubes and filled with a cation in the cube center; b) the most probable structural model of the $\text{Fe}^{3+}_{\text{trig}}$ center in chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystal. Only two anionic cubes, aligned along an $\langle 111 \rangle$ direction and joined by a split di-interstitial $\text{Cl}^- - \text{Cl}^-$ pair are shown.

The pulse annealing experiments at temperatures higher than RT, reported in this work, have shown that the $\text{Fe}^{3+}_{\text{trig}}$ center transforms into the $\text{Fe}^{3+}_{\text{cub}}$ center in the temperature range of 300–520 K. Such a transformation can be correlated with the thermally induced movement of the Cl^- interstitials, which was observed during annealing above RT in the case of the electron-trapped centers involving off-center Fe^+ ions [13]. Indeed, if a Cl^- interstitial is removed from the split di-interstitial structure, the remaining Cl^- interstitial occupies the “natural” position, in the corner of the anionic cube, resulting in a cubic symmetry of the Fe^{3+} center. Thus, the pulse annealing data for the hole-trapped Fe^{3+} centers confirm that the most probable structural model of the $\text{Fe}^{3+}_{\text{trig}}$ center involves a split di-interstitial $\text{Cl}^- - \text{Cl}^-$ pair. Further-on, we have shown that the $\text{Fe}^{3+}_{\text{cub}}$ center decays at higher temperatures ($T > 500$ K), most probably by recombination of the Cl^- interstitial with the thermally released hole from the Fe^{3+} ion. The evolution of the hole-trapped Fe^{3+} centers versus the annealing temperature above RT can be described as following:



In conclusion, the formation and transformation of the $\text{Fe}^{3+}_{\text{trig}}$ center is related with the presence and thermally activated movement of the interstitial Cl^- ions, which are easily produced by the chlorination process during growth of the fluorite $\text{SrCl}_2:\text{Fe}^{2+}$ crystal.

4. CONCLUSIONS

The thermal stability above RT of the hole-trapped Fe^{3+} centers, formed by X-ray irradiation at 80 K in chlorinated $\text{SrCl}_2:\text{Fe}^{2+}$ crystals, has been investigated by EPR. The trigonal Fe^{3+} center completely transforms into the cubic Fe^{3+} center in the temperature range of 300 - 520 K, with the release of a Cl^- interstitial ion, which further recombines with the hole released from the Fe^{3+} ion at higher temperatures, resulting in the decay of the cubic Fe^{3+} center up to 700 K. As in the case of the electron-trapped centers containing off-center Fe^+ ions, the formation and transformation of the trigonal Fe^{3+} center, containing off-center Fe^{3+} ions, is associated with the presence and thermally activated movement of the interstitial Cl^- ions, which are easily incorporated in the fluorite $\text{SrCl}_2:\text{Fe}^{2+}$ crystal by chlorination. The chlorination process during the initial $\text{SrCl}_2:\text{Fe}^{2+}$ crystal growth results in the formation of both electron- and hole-trapping Fe^{2+} centers with non-cubic symmetry, which involve off-center Fe^{2+} ions, of interest for future applications in information storage and quantum computing. It is interesting to note that a strong off-center displacement of the Fe^+ ions may also take place in the γ -irradiated Fe^{2+} doped ThO_2 crystal with fluorite structure, subjected to a strong local axial $\langle 001 \rangle$ crystal field [15]. This subject is waiting to be investigated.

Acknowledgements. This work was supported by ANCS, Core Program contract PN09-45.

REFERENCES

1. P. Garcia-Fernandez, F. Senn, C. A. Daul, J. A. Aramburu, M. T. Barriuso, M. Moreno, *Phys. Chem. Chem. Phys.*, **11**, 7545 (2009).
2. A. Trueba, P. Garcia-Fernandez, F. Senn, C. A. Daul, J. A. Aramburu, M. T. Barriuso, M. Moreno, *Phys. Rev. B*, **81**, 075107 (2010).
3. P. Gambardella, S. Rusponi, M. Veronese, S. S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P. H. Dederichs, K. Kern, C. Carbone, H. Brune, *Science*, **300**, 1130 (2003).
4. A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
5. J. M. Spaeth, J. R. Niklas, R. H. Bartram, *Structural Analysis of Point Defects in Solids. An Introduction to Multiple Magnetic Resonance Spectroscopy*, Springer Verlag, Berlin, Heidelberg, 1992.
6. J. M. De Siebenthal, D. Nicollin, H. Bill, *Chem. Phys. Lett.*, **58**, 317 (1978).
7. S. V. Nistor, M. Stefan, D. Schoemaker, *Phys. Stat. Sol.*, **b214**, 229 (1999).
8. H. Vrielinck, F. Callens, P. Matthys, S. V. Nistor, D. Ghica, D. Schoemaker, *Phys. Rev. B*, **64**, 024405 (2001).
9. D. Ghica, S. V. Nistor, H. Vrielinck, F. Callens, D. Schoemaker, *Phys. Rev. B*, **70**, 024105 (2004)
10. D. Ghica, S. V. Nistor, H. Vrielinck, F. Callens, E. Goovaerts, D. Schoemaker, *Phys. Stat. Sol. (c)*, **2**, 57 (2005).
11. S. V. Nistor, D. P. Lazar, H. Kaess, D. Schoemaker, *Solid State Commun.*, **104**, 521 (1997).
12. D. Ghica, S. V. Nistor, E. Goovaerts, D. Schoemaker, H. Vrielinck, F. Callens, *Phys. Rev. B*, **73**, 174103 (2006).
13. D. Ghica, S. V. Nistor, E. Goovaerts, *Phys. Stat. Sol. (a)*, **204**, 695 (2007).
14. W. Hayes (Ed.), *Crystals with the Fluorite Structure*, Clarendon Press, Oxford, 1974.
15. S. A. Marshal and S. V. Nistor, *Phys. Rev. B*, **6**, 24 (1972).