Lithium nanoparticles in lithium fluorite crystals

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Abstract. Using intensive optical absorption techniques we studied formation of lithium nanoparticles in LiF crystals under $^{60}$Co-$\gamma$-irradiation in the dose range of $10^5$–$10^9$ R at 300 K. At $10^6$ R the F-center absorption band 4.95 eV grows up D>3 and splits into a symmetric doublet of narrow resonances similar to s$^1$-metal nanoparticles surface plasmons. The maximal concentration $3.3 \times 10^{17}$ cm$^{-3}$ corresponds to ~14 nm distance between F-centers when they form F-F-pair and then M-center. Absorption band of divacancies 2.75 eV splits into triplet at $>10^7$ R, when Li$_n$ nanoparticles 3.26 eV are formed. Twinned LiF lattice provides the defects ordering and assembling of Li$_n$ nanorods with the size of 8 nm related with the peak electric conductivity at 240-280 K.

PACS: 71.70.-d ; 73.20Mf ; 73.22.-f

1. Introduction

Early experiments on radiation induced defect production in ionic LiF crystal with the widest gap (>14 eV) revealed besides point electron defects, such as anion vacancies (F-center, 252 nm) and divacancies (M-center, 445-450 nm), also ionic defects, such as molecular fluorine interstitials (H-center, 340-380 nm), vacancy aggregates (F$_i$-centers, 450, 518 nm), colloidal precursors (U-center, 495 nm) and colloids of various nature and sizes, such as impurity colloids (X-center, 275 nm) or intrinsic Li$_n$ ones (440, 530, 1000 nm) [1]. Aside the strong absorption of F-center an unknown band at 218 nm and a colloid center band at 265-285 nm were found [2].

After irradiation of LiF with thermal neutron fluency $3 \times 10^{17}$ cm$^{-2}$, plate-like Li particles of 5 nm size were discovered with transmission electron microscope, which grew to 100 nm after the fluency $10^{16}$ cm$^{-2}$ and following heating. Besides a prominent X-band at 280 nm, which belongs to impurity Mg colloids, a weak absorption band at 550 nm was also attributed to lithium colloids. The impurity colloids were formed easier at dislocations [3-5]. The defects induced at high fluencies were found to form an ordered substructure [6], which is very important.

Basing on Mie theory, describing extinction of small metal particles in transparent dielectric matrix, Li-colloid extinction in LiF was calculated at the sizes of spherical particles taken much less than the incident light wavelength $\lambda$, as shown in figures of [7]. The most intensive and narrow peak at 458 nm was attributed to colloids with a size <5nm (curve 0). When the size grows within 10-20 nm, the peak moves to 480 nm, its width broadens and its magnitude decreases in two times. If the colloid size increases within 25-60 nm, there appear doublet
bands characterized by a weak magnitude and broad width, with the both maxima moving towards a larger wavelength. The model of a colloid precursor as Li or impurity anion in an anion site was developed to explain W-center absorption at 270-275 nm [8]. Later the energy states of Li-colloid nucleus as F-center with interstitial Li atom in a fluorine vacancy were calculated [9]. Taking into account the exchange interaction between the electron trapped at F-center and 2s-electron of Li resulted in transformations of 1s level of F-center into singlet 1S + 3S terms of F(Li)-center, and 2p level into triplet 1P + 3P terms. Thus, in the related absorption spectrum the singlet transition 1s → 2p of F-center (250 nm) transforms into doublet: 1S → 1P 5.81 eV (213 nm) and 3S → 3P 4.53 eV (274 nm). The optical spectrometers available at that time made it difficult to observe the absorption band at 213 nm aside the intensive band 250 nm of F-centers, so only 270 nm could be seen and 250 nm should disappear to confirm this model.

Within the last decade the interest to metal nanoparticles in liquid has grown greatly because of their exciting properties, especially plasmonic resonant oscillations of their free electrons [10-12]. According to classic Mie theory, the surface plasmon frequency $\omega_s = \frac{\nu_f}{R}$, where $\nu_f$ is Fermi electron velocity and $R$ is a spherical nanocluster size, and the extinction line width $\Gamma \sim a/R$ [10]. Experiments confirm the line broadening for smaller Ag clusters, but the $\omega$ depends mainly on the permittivity of dielectric matrix $\varepsilon$ and the cluster concentration. By Mie-Gans theory, noble metal nanorods support two distinct plasmon modes: a longitudinal one moving toward red side and a transverse one to UV-side of spectra, with their frequencies dependent on the nanoparticle a/b aspect ratio [11]. This behavior differs from that for spheres of various sizes in [7]. Recently there appeared some articles on observation of nanosized metal colloids in a thin layer of LiF under fast Au ion irradiation that produced also nanosized ion tracks in the layer [13]. Broad complex absorption band at 2.3 - 3.3 eV was attributed to intrinsic Li colloids and a broader one at 4.4 - 4.6 eV to impurity Mn colloids. Since ion irradiation is very inhomogeneous, optical absorption of lithium colloids with growing size and probably shape should be studied thoroughly again with the use of homogeneous irradiation and fast reading highly luminous spectrometers and should be discussed as plasmon oscillations rather than just electron transitions in non-interacting point defect centers. Calculations in [7-9,11,12] should be tested experimentally.

The goal of this work was to study the formation of Li nanoparticles by assembling point defects in LiF crystal lattice under gamma-irradiation with the use of X-ray and optical spectroscopy.
2. Experiment

Available detector LiF crystals of the optical quality were taken for the experiment. The samples of 1 mm thickness were cleaved from a large crystal in (100) crystallographic planes so as to obtain a flat optical surface. With the use of X-ray fluorescent analysis at $^{109}$Cd source the element composition of LiF single crystals was determined.

Samples were irradiated at the $^{60}$Co radioisotope source of gamma-rays (1.17+1.32 MeV) in the wide dose range $10^5$-10$^9$ R at the rate of 526 R/s at 320 K in dry air. Defects were accumulated at 30 steps so as to hit the particular dose when charge exchange interaction between neighboring defects becomes strong and the spectral band should split, or one type of defects ($F_n$) transforms into another $F$(Li)-center [9]. So the task was to estimate $F$-$F$ distances. Since radiation defect absorption bands are known to be wide, with the intensity growing fast with the dose above the limited optical density $D=2$ for the most double-beam spectrophotometers [1-9], primary task was to choose the proper optical spectrometer to measure spectral dependence of optical extinction (absorption + scattering) above 2 up to 5 so as to see intensive excitonic and plasmonic peaks. It was a single-beam spectrophotometer SF-56A (LOMO, Russia) in the range of 190-1100 nm with fast reading Si-photodiode array and the pc code FORT, the admitted absolute error less than ±1 %. Here we used the mode of the maximal slit opening to 6 nm that ensured registration of $D$ up to 5 due to significant increasing the intensity of incident light beam. Optical spectra were measured 5 min. after each irradiation step so as to detect unstable optical centers ($M, R_2, V_k$, Li-colloid and $H$-interstitial [1]).

According to Smakula-Dexter formula $n_F = 9.48 \cdot 10^{15} D_F$ adapted for LiF (n=1.35) [13,14], the number $N$ of color–centers per cm$^2$ was determined at each dose, and volume concentrations were calculated both for $F$–centers (250 nm) and $M$–centers (445 nm).

X-ray diffraction techniques were used for structure and phase analysis at nanoscale. For this task a serial diffraction meter DRON-3M (Russia) was upgraded for narrowing the apparatus function and increasing of the beam intensity. The improved collimation system provided two times increase in the signal-to-background ratio at small and medium scattering angles. It allowed us to select the low angle scattering background and weak narrow selective reflections, broadening and splitting of the basis lattice reflections into doublets and triplets, which determine the character of local stresses and twinning, respectively [15]. Nanoparticle sizes were evaluated by Selyakov-Scherrer formula with an experimental error below 10 %.

DC Electric conductivity was measured with 2-probe technique at 25 Volt within 80-400 K.
3. Results and discussion

3.1. Element composition of crystals

The most prominent cation impurity was found to be Cu 0.02 wt% i.e. $6 \times 10^{17}$ cm$^{-3}$ (the rest Ti, V, Cr, Mn, As, Au are below 0.01%). Since Cu$^+$ has the ion radius of 0.091 nm, which is larger than that of Li$^+$ 0.073 nm, it causes the local lattice deformation around, which can be compensated with an adjacent anion vacancy. The only anion impurity was Br$^-$ < 0.01%, but due to a larger difference in ionic radii i.e. 0.182 nm vs 0.119 nm for F$^-$ ion it causes a stronger local lattice deformation, than Cu$^+$, that can be compensated with an anion vacancy too. Therefore in non-irradiated sample there is a weak semi-band at the spectral edge 190 nm [1-6]. And under ionizing gamma-irradiation we expect charging of these vacancies i.e. creation of F- centers near the impurities, the concentration of which should saturate maximum at $6 \times 10^{17}$ cm$^{-3}$.

3.2. X-ray diffraction analysis of structure and phase

The powders for structure studies were made by mechanical abrasion of small LiF single crystals. The obtained grain sizes were within 14 - 21 μm. Part of the samples were irradiated with $^{60}$Co-gamma-source to doses $10^7$, $10^8$ and $10^9$ R in the dry air at 300 K. Measurements of the same mass samples were done at 300 K. Figure 1 (left) shows X-diffraction pattern on the non-irradiated LiF powder, which consists of an inelastic background and 6 selective reflections of different intensities over it, which belong to LiF lattice. The basic singlet 200-reflection with d/n
spacing 0.2011 nm is the most intensive ($I \times 10^4$ pulse-sec$^{-1}$). Besides at small angles $2\Theta = 15–32^\circ$ very weak broad diffuse scattering is due to structure fragments with non-saturated bonds distributed chaotically in subsurface layers of grains. Figure 1 (right) shows the pattern for LiF irradiated to the maximal dose $10^9$ R. Comparing to non-irradiated one, all the selective peaks of the lattice have widened and got lower intensities: that of (200) has decreased in 2 times, the rest by 6-26 %. Such intensity losses are due to radiation induced “evaporation” of fluorine (i.e. radiolysis). Besides, the non-elastic background has got a non-even shape with weak steps, wells and hills, indicative of F emission preferably from the subsurface sites with a high potential, where self-assembling of Li metal clusters (then Li lattice) takes less energy.

The diffraction peaks of metallic Li particles are expected to occur at $2\Theta = 32–40^\circ$, 48-56$^\circ$ and 68–75$^\circ$. However the spectrum shows no signal in the non-irradiated sample. Since the volume of subsurface layers is a negligible part of the total bulk, the reflection intensity for metal Li lattice must be very weak, let alone its small atom number 3. Nevertheless such a selective reflection (200) with $d/n = 0.1758$ nm from Li crystal particles could be observed experimentally at 52$^\circ$ only in the heavily irradiated ($10^9$ R) LiF sample, as seen in Fig.1 right. Having the same orientation (200) and cubic symmetry as matrix LiF crystal, radiation induced Li nanocrystals form coherent metal-dielectric interfaces. The characteristic size of Li nanocrystals estimated by Selyakov-Scherrer expression is 8 nm, which confirms the calculated values [7,11].

Twinning of LiF lattice with (100) orientation occurs within (111) plane [6,15]. Nanotwin length was estimated from splitting of the basic reflection (200) into triplet as 100 nm in non-irradiated and 20-30 nm in irradiated crystals. In the case of wet irradiation the diffuse band at 26 grad is responsible for particles with an average size < 5 nm, while a weak narrow peak at 57 grad is attributed to LiOH nanocrystals oriented at (112) with a length of 28 nm [15].

### 3.2. Optical extinction spectra

We found recently [16], that the absorption band at 250 nm ($F$-center) increases after gamma-irradiation in the dose range of 0.09 - 0.64 MR up to the optical density $D=3$, while its width narrows from 0.89 to 0.72 eV. It is characteristic for spherical nanoparticles [11]. Fig.2 left shows splitting of the band 250 nm into symmetric doublet of 240 and 260 nm with intensities $D>3$. At concentration $3 \times 10^{17}$ cm$^{-3}$ (less than Cu) the distance between neighboring $F$-centers becomes 14 nm, which is less than the size of Li exciton 20 nm [1]. The reduced line width of the doublet means a lower rate of the plasmon decay, and the extinction is dominated by absorption [11].
There also appears a weak band at 220 nm which was ascribed either to self-localized excitons or to X-centers [1-5]. The following irradiation with the small dose steps caused moving of the doublet components away each from other with descending intensity of the long-wave component, as it can be seen in Fig.2 right and calculated in [7]. At the dose of 7.5 MR the wavelengths of the doublet components reach the values of 220 and 270 nm that confirm well the F-band splitting calculated in [9]. Besides, simultaneously there emerged well known band at 445 nm attributed to M-centers and hardly resolved band about 460 nm, which is ascribed by various authors either to \( F_4 \) aggregate centers or Li colloids <5 nm [1,7]. Our measurements showed that divacancy based M-centers appear only after splitting of 250 nm band due to transformation of F-center into \( F-F \)-pair by the model of [9]. It is reasonable to assume that the observed behavior of the doublet with the dose grows (i.e increase in splitting) is due to shortening of the distance between F-centers in pair and the related increase in the exchange interaction. Fig. 2 right also shows formation of \( F_3 \) (320 and 375 nm) and \( F_4, F_5 \) aggregates (500-700 nm) at the following dose increase to 20 MR. After growing to \( D>3 \) the band at 445 nm splits asymmetrically and unstably, when the \( M-M \)-center distance shortens to 22 nm. Since the aggregates may gain various configurations of different stability [11], the measurements were repeated many times within a few hours, days. The broad weak band about 620 nm turned out unstable and annealed in 3 hours at 300 K. It may be responsible for the dominating light scattering as \( 1/\lambda^4 \) from large nanoparticles of 50 nm as calculated in [7], and may be attributed to an unstable linear \( F-F-F-F \) configuration which transforms into more stable square of \( 4F \)-centers, where Li colloid is formed. \( F_3 \)-centers grow quite slow due to their non-stability.
Considering $F$-aggregate centers as places for Li colloid generation, it seems reasonable to implement the ratio of a longitudinal plasmon wavelength $\lambda$ and the related length of a metal nanorod $L$. In the case, when only dipole oscillations contribute to the optical density $D$, the ratio is $\lambda = 10L$, so the observed peaks correspond to $L$ changes within 27-30 nm, which is in a good agreement with the estimation of the twin length from X-ray diffraction measurements (fig.1).

3.3. Electric conductivity
Thermally activated direct electric current (DC) of non-irradiated and irradiated LiF samples was measured with 2-probe technique at applied 25 V as shown in Figure 3 (1kGy $= 0.1$ MR).

Prior to irradiation there occurred only ion conductivity at $T > 350$ K. Irradiation induced peak conductivity around 250 K means delocalization of charge carriers from traps, their depth increasing with the dose growth, that make a 3D-conducting cluster. When the Li nanoparticle size $L$ grows within 10-50 nm, the coulomb barrier for single electron transition decreases.

4. Conclusions
Mie theory based Radchenko [7] calculations of extinction dependent Li-colloid size and Lobanov’s [9] model of $F(Li)$ doublet absorption were confirmed well in our optical experiments. Broad singlet absorption bands of isolated $F$- and $M$-centers grow up to $D \approx 3.5$ at 10 times different doses then split into doublet and triplet due to $F-F$ and $M-M$-pair centers formation below the critical distances 14 and 22 nm, respectively, when their exchange interaction and
oscillator strength is maximal. The maximal concentration of the pair centers is 2 times less than that of Cu impurity. So Li colloids are formed around Cu at the existing anion vacancies. Irradiation dose determines the size of Li-nano-particles >8 nm by self-assembling from the point defects and their arrangement into nanostructure of super-lattice type by changeably twinning. Optical density $D$ and wavelength $\lambda$ of longitudinal and transverse plasmon resonances depend on Li-nanorod aspect size and charge, and hence the matrix permittivity $\varepsilon$. Free electrons are confined in nano-Li in LiF matrix at the coherent metal-insulator interface oriented in (200) plane. When Li nano-crystals form 3D- cluster, electric conductivity emerges at 240-280 K possible due to single electron transport through the interface. Non-linear properties of gamma-irradiated LiF (passive Q-switch mcs-ps for YAG-Nd) [1,15] come from Li-nanorods ordered with twin nanostructure rather than $M$- or $F_2$ centers. Other applications of LiF with nano-Li sublattice are possible, such as plasmon-enhanced resonant optical forces and also nanophotonic devices.

**Acknowledgments.** The researches are supported by national grant FA-F2-F068.

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Supplementary data attachments to enhance the online versions of the article consist of data files, tables of extra information and extra figures.

\textit{XDA of LiF powder}. \(\beta\)-component of the main peak (200) is seen at 40.7°. The rest selective peaks also belong to LiF structure: (111) \(d/n = 0.2327\) nm at \(2\Theta = 38.7°\), (220) 0.1224 nm 65.7°, (311) 0.1213 nm 78.9° and (222) 0.1162 nm 83.1°.

![Figure 1-s. X-ray diffraction fragment of (200) peak shoulder: 1- non-irradiated, 2- irradiated LiF powder.](image)

Optical reflection spectra are not applicable in this case, since expected nanoparticle sizes must be much less than incident wavelengths. So optical absorption of 1 mm thick LiF plate with (100) orientation was measured prior and after gamma-irradiation to the indicated doses. Figures 2 A,B,C were published in our paper in: Reports of Uzbekistan Academy of Sciences 2011, # 1.
Figure 2-s. Optical absorption spectra. A: the lowest curve – non-irradiated, the magnitude of band at 250 nm grows with increasing the irradiation dose to 0.63 MR. B: the band splitting increases with the dose growth to 1.8 MR. Band at 450 nm is attributed to M-centers. C: The
bands at 210 nm and 450 nm grow up and begin splitting at the dose 20 MR, when laser
generation becomes effective. Table shows calculated concentrations $N_F$ of F-centers

| Dose $10^5$ R | $N_F$ (250 nm) $10^{17}$ cm$^{-3}$ | $d$ between $F-F$ centers nm | Dose, $10^5$ R | $N_M$ (445 nm) $10^{16}$ cm$^{-3}$ | $d$ between $M-M$ centers nm |
|---------------|-----------------------------------|-----------------------------|---------------|-----------------------------------|-----------------------------|
| 0             | 0                                 | –                           | 8,1           | 0,64                              | 54,3                        |
| 0,9           | 0,97                              | 21,7                        | 9,9           | 1,14                              | 44,8                        |
| 1,8           | 1,33                              | 19,5                        | 18            | 1,61                              | 40,0                        |
| 2,7           | 1,63                              | 18,2                        | 37            | 2,24                              | 35,8                        |
| 3,6           | 1,97                              | 17,2                        | 55            | 2,92                              | 32,9                        |
| 4,5           | 2,25                              | 16,4                        | 75            | 3,71                              | 30,4                        |
| 5,4           | 2,26                              | 16,3                        | 93            | 5,69                              | 26,4                        |
| 6,3           | 2,74                              | 15,4                        | 110           | 6,67                              | 25,1                        |
| 7,3           | 3,33                              | 14,5                        | 200           | 9,64                              | 22,2                        |