Damage and track morphology in LiF crystals irradiated with GeV ions

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The nature of the radiation damage in lithium fluoride crystals irradiated with various ion species between nickel and uranium was studied by techniques such as optical absorption spectroscopy, small-angle x-ray scattering (SAXS), and chemical etching complemented by annealing experiments. The results indicate a complex track structure and defect morphology: Single defects such as F and F_2 centers are produced in a large halo with a radius of several tens of nanometers around the ion trajectory. Above a critical energy loss of about 10 keV/nm, new effects occur within a very small core region of about 2–4 nm in diameter, resulting in a strong anisotropic x-ray scattering and in the etchability of tracks. It is concluded that in this core region, the defects are complex aggregates such as small Li colloids, and fluorine and vacancy clusters. Using Monte Carlo calculations, the spatial distribution of energy deposited around the ion trajectory is compared with the track radius as extracted from the SAXS experiments. For all ion species, this radius corresponds to a critical dose, which can be regarded as a threshold for the creation of defect aggregates in the core region. [S0163-1829(98)01141-2]

I. INTRODUCTION

The creation of defects in lithium fluoride and in other alkali halides under various types of radiation (photons, electrons, neutrons, and ions) has been intensively studied during the past decades. Without a doubt, the problem has owed its attraction to the simplicity of the ionic lattice of such crystals and the ease with which the structure can be damaged. The radiation damage occurs mainly in the anion sublattice. The primary defects are created via self-trapping of excitons and the subsequent nonradiative decay. At room temperature, the most significant type of defects are F centers (an electron on an anion vacancy), F_2 centers, and the complementary hole centers.¹⁻⁴ Depending on the material, such point defects subsist up to a very high level of energy deposition, which allows the study of special effects, for instance, the deviation from linearity in the defect production, saturation effects, and the formation of complex aggregates (color centers, molecular anion clusters and vacancy clusters, metal colloids, etc.). Large aggregates and macrodefects can be created only above a critical defect concentration and at irradiation temperatures where diffusion of single point defects is possible.5-7

The aim of this study is to gain a better understanding concerning the specificity of the damage produced in LiF when irradiated with swift heavy ions. At energies above about 1 MeV/*u*, elastic collisions between the projectile ion and the target atoms can be neglected. Therefore, the interaction of high-energy ions is characterized by almost pure electronic excitation of the target atoms. The primary ionization and excitation processes and the following electron cascades occur within a very short time of 10^{-17} to 10^{-14} s, being much shorter than the time necessary to create defects via lattice relaxation ($10^{-12}-10^{-11}$ s). Another significant difference to low ionizing radiation (e.g., electrons, gammas, or x rays) is the final distribution of the energy deposited is not homogeneous, but each individual ion deposits its en-

ergy with an approximately $1/r^2$ dependence on the radial distance from the trajectory.⁸ Such a dose gradient could have a strong influence on the defect creation mechanisms and on the nature of the damage. In particular, close to the ion path, extremely high local doses are reached, unattainable by any other energy deposition process.

In a wide range of materials, the irradiation with energetic heavy ions results in new effects. On a nanometer scale, ions induce modifications such as local phase transitions, amorphization, or mechanical stress.^{9–15} In order to describe the experimental results obtained in many different material classes, various models are considered. However, the discussion is controversial, and the contribution of elementary processes (excitons or electron-hole recombination^{1,2}) and collective excitation processes (e.g., Coulomb explosion^{16,17} or thermal spike^{18,19}) is still an open question.

While special ion-induced effects have been studied in a wide range of insulating materials (e.g., polymers²⁰⁻²² and oxides^{23,24}), only a few investigations have been made in ion- irradiated alkali halides. In most cases, lighter ions of rather low-stopping powers were used.^{25–28} Perez *et al.*²⁵ studied LiF crystals, irradiated at room temperature with Ne, Ar, Kr, and Xe ions in the energy regime between 30 and 60 MeV/u. By optical absorption spectroscopy it was shown that the main defects in tracks are F and F_2 centers. Moreover, for various alkali halides irradiated with heavy ions at low temperatures, Balanzat et al.²⁶ demonstrated that the resulting exciton luminescence spectra and the dependence of the efficiency on temperature are the same as under x-ray or optical excitation. These results gave clear evidence that electronic excitations induced by ions play an important role for the intrinsic luminescence and defect creation.^{1,2} At that time, no special investigations of more complex defects (e.g., aggregates of F centers or colloids) were made.²⁹ However, much earlier, Young had observed that latent tracks of uranium fission products can be revealed by chemical etching.³⁰ This technique is based on the increased chemical reactivity of the damaged zone along the ion path compared

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to the unirradiated surrounding crystal matrix. Interestingly enough, the etching of a single ion track and of an etched dislocation lead to the same shape of etch pit.³¹ Recently, we complemented this early observation by a systematic study of track etching using various heavy ions in the energy regime of several MeV per nucleon.^{32–34} It was found that track etching is only possible if the ions have surpassed a critical energy loss of about 10 keV/nm. Although the nature of this etchable damage has not been identified, it is supposed to be related to the formation of larger defect aggregates (*F*-center clusters, Li colloids, fluorine, and vacancy clusters). This assumption is supported by earlier findings that under high-dose irradiation with thermal neutrons only larger defect aggregates but not single defects can be etched.⁶

In this paper, we present the results of a series of investigations providing a better understanding of the damage morphology and microstructure of ion tracks in LiF. We complement earlier spectroscopic studies of F- and F_2 -centers using light ions^{25,27} by experiments with much heavier ions. Furthermore, small-angle x-ray scattering (SAXS) measurements were performed from which the diameter of the ion tracks can be deduced. In order to test the thermal stability of the damage induced, irradiated crystals were annealed step by step and analyzed by both techniques. We are also reporting about Monte Carlo model calculations determining the spatial dose distribution perpendicular to the ion trajectory. Using these simulations, a critical dose will be deduced, which is required to create a damage sufficiently large to induce an anisotropic SAXS pattern and the etchability of tracks.

II. EXPERIMENTAL METHODS

A. Irradiation

Single crystals of high-purity lithium fluoride were cleaved into platelets of a thickness between 200 μ m and 1 mm and of an area around 1 cm^2 . The crystals were irradiated with U, Bi, Pb, Au, Xe, Kr, Se, Zn, and Ni ions of a specific energy of up to 11.4 MeV/u at the linear accelerator UNILAC of the GSI (Darmstadt, Germany) and with Pb of 4 MeV/u at the medium energy line of GANIL (Caen, France). In several cases, aluminum degraders of different thicknesses were used in order to decrease the initial energy of the ions. All irradiations were performed at room temperature and under normal incidence to the cleavage plane of the crystals. The total fluence of the ions varied between 5 $\times 10^9$ and 10^{12} ions/cm². In order to avoid an increase of the sample temperature, the flux of the ions was limited to about $5 \times 10^8 \text{ s}^{-1} \text{ cm}^{-2}$. The most relevant parameters of the irradiations are listed in Table I. The given ion range and the electronic energy loss $(dE/dx)_i$ at the crystal surface were calculated with the computer code TRIM 89.35 The projected range of the ions was in all cases less than the thickness of the crystals, so that the ions were stopped in the crystals. For that reason, we used the energy loss averaged along the full ion path, by dividing the initial energy by the range of the ions as given by the TRIM code.

TABLE I. Parameters of the ion irradiations.

Ion	Energy (MeV/u)	Range (µm)	$(dE/dx)_i$ (keV/nm)	Mean (dE/dx) (keV/nm)
⁵⁸ Ni	11.4	96	5.4	6.9
⁶⁸ Zn	11.4	96	6.0	8.1
⁸² Se	11.4	104	7.4	9.0
⁸⁴ Kr	11.4	98	8.0	9.8
¹³⁰ Xe	11.4	91	14.3	16.3
¹⁹⁷ Au	11.4	96	24.0	23.4
	5.4	49	27.0	21.7
²⁰⁸ Pb	11.4	96	24.9	24.7
	5.4	49	27.9	22.9
	4.0	38	27.9	21.9
²⁰⁹ Bi	11.4	95	25.4	25.1
	10.9	91	25.7	25.0
²³⁸ U	11.4	100	28.8	27.1

B. Optical spectroscopy

The creation of color centers was studied using a UVvisible double-beam spectrometer (ATI Unicam UV4). Absorption spectra of the irradiated crystals were typically recorded in the spectral range between 200 and 600 nm where the absorption of the electron color centers are localized (hole centers that are stable at room temperature, have their absorption bands in the vacuum ultraviolet spectral region). As quoted in the literature, the absorption band of *F* and F_2 centers was found at a wavelength of 245 and 445 nm, respectively. The concentration n_F (cm⁻²) of the *F* centers and n_{F_2} (cm⁻²) of the F_2 centers was determined with the Smakula-Dexter formula using an oscillator strength of, respectively, 0.6 and 0.3:^{25,36-38}

$$n_F = 9.48 \times 10^{15} \times A,$$
 (1)

$$n_{F_2} = 4.42 \times 10^{15} \times A,$$
 (2)

where $A = \ln I_0/I$ is the optical absorbance at the band maximum. If we are interested in the volume concentration N_F and N_{F_2} , i.e., the number of *F* and F_2 centers per cm³, it has to be taken into account that the color centers are created in a crystal layer of a thickness that corresponds to the ion range R ($N_F = n_F/R$).

C. Small-angle x-ray scattering (SAXS)

In order to complement the results obtained by optical spectroscopy, which mainly allowed us to analyze single defects, we also performed small-angle x-ray scattering experiments. They were carried out with a setup in transmission geometry, in most cases with an angle of 45 ° between the ion trajectories and the x-ray beam. The distance from the sample holder to the position-sensitive area detector (10 \times 10 cm²) was around 120 cm. We used the $K\alpha$ - Cu radiation of a rotating anode generator (49 kV and 200 mA) with a pinhole collimation. The efficiency correction, the smoothing of the scattered intensity, and the analysis of the SAXS data was performed with the GADDS software (Siemens).

For the analysis of the intensity distribution, it was assumed that each track can mathematically be described by a cylinder of a Gaussian radial density variation with the z axis of the cylinder corresponding to the ion trajectory. For such a configuration, the intensity distribution $I(k_r, k_z)$ in the reciprocal space is given by

$$I(k_r, k_z) = \delta \rho^2 \times 4 \, \pi^2 \times a^4 \times \sin^2(k_z \times R/2)/k_z^2$$
$$\times \exp(-k_z^2 \times a^2/2). \tag{3}$$

where *R* is the length of the cylindrical track corresponding to the ion range. k_z and k_r are the length of the momentum vector parallel and perpendicular, respectively, to the ion path. Here, k_r is obtained from the relation $k_r = 4 \pi / \lambda \sin \phi$ where 2ϕ denotes the scattering angle and λ (1.54 Å) is the wavelength of the x-ray beam. $\delta \rho$ is the maximum electron density difference between the damaged material of the track and the virgin crystal, and *a* defines the Gaussian radius of the track at which $\delta \rho$ decreases to 1/e.³⁹

D. Chemical etching

Since specific details of track etching in LiF have been published elsewhere,³² we give only a short description of the experimental conditions. As etchant, a solution of concentrated hydrofluoric acid (50 vol%) and glacial acetic acid (50 vol%) saturated with ferric fluoride (FeF₃) was used, as recommended in Refs. 30 and 31. On the irradiated crystal surface, successful etching leads to the appearance of a pyramidal-shaped etch pit for each individual track. Some of the samples were cleaved prior to etching perpendicular to the sample surface. In this geometry, the damage along the ion trajectories is revealed as long striated structures.³²

III. RESULTS

A. Creation of F and F_2 centers

In LiF, the irradiation with heavy ions leads to a strong coloration of the crystals between yellow and dark brown depending on the fluence and range of the ions. The depth of the colored zone was compared with the ion range as calculated by the TRIM code.³⁵ At the given accuracy of our optical microscope, it was for all ions between 10% and 20% smaller than the projected range. This effect is in agreement with the experience that the TRIM code generally overestimates the ranges of ions in this energy regime.^{32,40} A quantitative evaluation of the color centers was performed with the optical spectrometer analyzing the absorption peaks of the F and F_2 centers at 245 and 445 nm, respectively. A typical spectrum is shown in Fig. 1 (curve a) for a crystal irradiated with 10^{10} Bi ions/cm² at 11.4 MeV/u. At higher fluences, the spectrum became more complex, exhibiting peak shoulders at around 315, 375, 518, and 540 nm, as demonstrated in Fig. 1 (curve b) for a sample irradiated with 2×10^{11} Bi ions/cm² at 10.9 MeV/*u*. These bands can be assigned to color center aggregates such as F_3 centers (316, 374 nm), F_4 centers (518, 540 nm),⁴¹ and possibly to Li colloids. The position of the colloid absorption bands are expected in the range between 450 and 500 nm,^{5,42} and therefore they overlap with the bands of other color centers. It should be mentioned that the dependence on shape and size



FIG. 1. Absorption spectra of LiF crystals irradiated with Bi ions at a fluence of (a) 10^{10} cm⁻² and (b) 2×10^{11} cm⁻².

of the colloids is not known in sufficient detail to perform a straightforward analysis of the spectra at high fluences.

In the following section, we will focus mainly on the evolution of F centers in samples irradiated at lower fluences. The analysis was in most cases limited to ion fluences below 2×10^{11} ions/cm², because at a typical thickness of the irradiated layer of about 100 μ m, the optical absorbance became too high to be measured. The number of F centers per single track is about 10^5 and 10^6 for Zn and U ions, respectively.

Figure 2 shows the number of F centers as a function of the fluence for some selected ion species. In the low fluence regime, the F-center concentration exhibits a linear increase, while at sufficiently high fluences, it saturates. This observation gives evidence that overlapping of individual ion tracks occurs. From the saturation curve, we can estimate the radial dimension around the ion path in which F centers are created by using the model proposed by Thévenard et al.²⁷ In order to simplify the problem, the distribution of F centers is represented by a homogeneous cylindrical volume around the ion trajectory in which the concentration of F centers is saturated. Whenever two neighboring tracks overlap, single F centers are assumed to aggregate and the creation of additional single F centers is neglected. Depending on the size of the track, the concentration of F centers as a function of the fluence will reach saturation, when the entire crystal surface is covered by tracks. The mathematical description of this evolution is given by



FIG. 2. The concentration of *F* centers as a function of the ion fluence for samples irradiated with Zn (11.4 MeV/u), Au (5.5 MeV/u), and Pb (11.4 MeV/u) (the data point at the highest fluence of the Zn irradiation is not shown). The curves are fits to the data based on Eq. (4).

TABLE II. Track radius r_F and saturation concentration n_s for various ion species.

Ion (MeV/ <i>u</i>)	r _F (nm)	$(10^{16} \text{ cm}^{-2})$
Zn (11.4)	15 (1)	5.4 (5)
Au (5.5)	20 (2)	3.3 (2)
Pb (4.0)	19 (1)	3.6 (1)
Pb (11.4)	29 (2)	4.5 (2)

$$n_F = n_s [1 - \exp(-\pi r_F^2 \times \phi)] \tag{4}$$

where $n_F(\text{cm}^{-2})$ is the experimentally observed number of *F* centers per unit of the sample surface irradiated with an ion fluence ϕ (ions/cm²), n_s (cm⁻²) is the saturation density of *F* centers, and r_F is the radius of the cylindrical region in which single *F* centers dominate. This kind of data analysis was possible for samples where the irradiation conditions allowed us to reach sufficiently high fluences such as for the Zn (11.4 MeV/*u*), Au (5.5 MeV/*u*), and Pb (4.0 and 11.4 MeV/*u*) ion beams.

The curves in Fig. 2 result from a fit of the experimental data by means of Eq. (4). The corresponding track radii r_F of various ions are given in Table II, where the listed errors correspond to the fit quality and do not include systematic uncertainties of the experiment. It should be noted that the deduced parameters represent integral average values, not taking into account that the track size may vary along the depth in the crystal due to a dependence on energy loss or ion velocity. We found that the radius r_F increases with the atomic number and with the velocity of the ions from 15 nm for Zn up to almost 30 nm for Pb.

Another interesting parameter deduced from the fit of the *F*-center curves in Fig. 2 is the saturation level n_s (Table II) between 3 and 5×10^{16} cm⁻². This corresponds to a volume concentration of about 10^{19} cm⁻³ and a mean distance between two *F* centers of the order of 70 Å (i.e., 17 lattice distances). It is interesting to see that for the Au and Pb ions of lower energy, the saturation concentration is slightly smaller than for the faster Zn and Pb ions. The value is in good agreement with earlier observation using lighter ions.^{25,27} Furthermore, for LiF and other alkali halides under gamma or electron irradiation in the high dose regime, such a concentration of *F* centers is typical for the onset of aggregation processes.^{7,27,41-46}

A data analysis of F and F_2 centers up to complete saturation was possible only for one set of samples irradiated with Pb ions of an energy of 4.0 MeV/u. The low energy has the advantage of producing F centers only in a thin region of 38 μ m below the crystal surface, allowing us to follow the concentration up to very high fluences. Under this condition, we could study also the evolution of the F_2 centers, which is difficult at low fluences mainly because of the low production rate in combination with a small oscillator strength. It became evident that the concentration of the F_2 centers saturates at a higher fluence than single F centers (Fig. 3).

For fluences below about 10^{10} ions/cm², the concentration of F_2 centers is directly proportional to the square of the *F* center concentration $[N_F = \text{const} \times (N_{F_2})^2]$. The exponent



FIG. 3. Concentration of F centers (circles) and F_2 centers (triangles) as a function of the fluence of Pb ions of 4.0 MeV/u.

of 2 gives evidence that in the nonoverlapping track regime, F_2 centers are formed by pairing of randomly neighboring *F* centers.

B. Small-angle x-ray scattering

The scattering patterns of all irradiated crystals studied by SAXS exhibited an anisotropic intensity distribution. Figure 4 shows a typical scattering pattern on the 10×10 cm² position-sensitive detector for a crystal irradiated with 10^{10} Xe ions/cm² (11.4 MeV/*u*). The high contrast along the vertical axis of the detector plane reflects the electron density difference of the damage in the tracks and the surrounding unirradiated crystal. Compared to the heavier ions, the contrast of the anisotropy of the scattering pattern of the Zn and Se ions was extremely weak, so that the data could not be evaluated quantitatively.



FIG. 4. Anisotropic scattering pattern of a crystal irradiated with 10^{10} Xe ions/cm² (11.4 MeV/*u*) on the 10×10 cm² position sensitive detector. The gray scale is a measure of the x-ray intensity. The light spot in the center originates from the catcher of the primary x-ray beam.



FIG. 5. The logarithm of the scattered intensity as a function of the square of the scattering vector k_r for crystals irradiated with Xe and Au ions.

Whenever possible, the scattered intensity was analyzed along the vertical cut through the center of the detector plane. Using a Guinier presentation (Fig. 5), the logarithm of the scattered intensity $I(k_r)$ was plotted as a function of the square of the scattering vector k_r . By fitting a straight line to the scattering data, the Gaussian track radius was determined from the slope according to Eq. (3). From the excellent fit of a straight line, we conclude that the geometry of the damage along the ion path is well represented by a cylinder. Further evidence for this shape is provided by SAXS experiments where the x-ray beam was oriented perpendicular to the ion tracks. Under this condition, we obtained the same anisotropic scattering pattern indicating that the damage has a quasicontinuous structure rather than consisting of isolated damage zones. In this latter case, e.g., spherical defects would lead to an isotropic scattering pattern that was not observed here.

Figure 6 displays the SAXS radius of various ion species increasing as a function of the mean energy loss from 1.0 nm for Kr ions to 1.8 nm for U ions. Each data point represents a mean value of several measurements using different crystals. Within the studied fluences regime between 5×10^9 and 2×10^{11} ions/cm², no significant influence on the radius of a given ion was observed. It should be pointed out that for this



FIG. 6. Track radii of various ion species obtained from SAXS experiments as a function of the mean energy loss. The initial energy of all ion species was 11.4 MeV/u.



FIG. 7. Optical absorption spectra of LiF crystals irradiated with Pb 11.4 MeV/u ions at a fluence of 10^{11} ions/cm²: (a) before annealing; (b) after annealing at 300 °C for 20 min.

analysis, the density profile of the tracks was assumed to have a Gaussian distribution. If we would consider a density profile with a steplike transition instead, the track radius deduced from the same scattering data would be larger by a factor of 1.4.

Comparing the data with those obtained from the optical analysis of the F centers, it is evident that the SAXS radii are about one order of magnitude smaller. Obviously, tracks in LiF have a microstructure, i.e., a small core of a few nanometers surrounded by a much larger halo consisting mainly of single F centers and hole centers. Since SAXS does not allow the analysis of the damage giving rise to anisotropic x-ray scattering, the question about the nature of the defects remains open.

C. Annealing behavior

In order to investigate the thermal stability of the defects in ion tracks, irradiated LiF samples were annealed under argon atmosphere for 20-30 min in the range from room temperature to 500 °C. The behavior of the defects was studied by absorption spectroscopy, chemical etching, and in some cases by SAXS. For samples irradiated with a low fluence of around 5×10^9 ions/cm², the concentration of single F centers decreased by a factor of 2 at a temperature of about 240 °C. From an Arrhenius plot, the activation energy for annealing of F centers was determined to be about 0.35 eV. This value corresponds well with the activation energy of temperature-induced mobility of hole centers^{41,45} and suggests that annealing occurs via recombination of F centers and hole centers. During the annealing procedure, the F_2 centers disappeared at a lower temperature than single F centers. The situation was different for samples irradiated at higher fluences. Already before the thermal treatment, the absorption spectra of such samples exhibited a complex band structure due to aggregated defects (e.g., F_3 and F_4 centers), which result from overlapping of individual ion tracks (Fig. 1). At around 300 °C, we observed a transition from the complex spectrum to a spectrum with only one broad peak at 275 nm (Fig. 7). Without changing the position of the maximum and the halfwidth of the peak, this band was stable up to 360 °C. At higher temperatures, its intensity started to decrease and finally, the signal disappeared at 450 °C. From this observation, we conclude that the band can be ascribed to rather stable aggregates formed due to increased diffusion of single F centers at temperatures above 300 °C. The authors of Refs. 5 and 47 also report on a band at 275 nm obtained after annealing of irradiated LiF crystals (ion implantation and thermal neutrons). Since they could not observe any signal due to electron spin resonance, they conclude that this band corresponds to nonparamagnetic aggregates.

We also tested the etchability of tracks on the surface of irradiated crystals and on a cleaved plane along the ion trajectories. In contrast to the color centers, the etchability was maintained to much higher temperatures. Below $300 \,^{\circ}$ C, the etch pits of crystals irradiated with various ions between 10^{6} and 10^{7} ions/cm² exhibited no significant change. Between 300 and $400 \,^{\circ}$ C, the number of etch pits continuously decreased with the disappearance of mainly smaller etch pits. Finally, for temperatures above $400 \,^{\circ}$ C, we could not find any etch pits.

Results from SAXS experiments of annealed crystals indicate a very similar behavior: Up to 300 °C, the SAXS radius did not change significantly compared with the untreated tracks. Between 300 and 400 °C, the anisotropy of the scattered intensity could still be identified but was too weak to be evaluated, and above 400 °C the typical pattern disappeared completely. Obviously, the stability of the damage responsible for the SAXS pattern and the etchability of tracks is maintained up to a higher temperature than *F* centers.

D. Correlation of the radial dose distribution with SAXS radii

In order to quantify the radial extension of the radiation damage, the spatial distribution of the deposited energy has to be included. Since this parameter is not provided by the TRIM code, we used the Monte Carlo simulation code TRK,⁴⁸ which models the interaction of the ions with the electrons of the target by the binary encounter approximation. Cross sections for elastic scattering, ionization, and excitation of the target atoms by secondary electrons were taken from semiempirical formulas. Since detailed experimental data exist only for collision processes of ions in gas targets, the calculations were performed for ions in water vapor. The results were adjusted to LiF taking into account the difference in density, mass, and atomic number, however, without considering the electronic structure of the solid. The evolution of the electron cascade was calculated by treating each ionizing event individually, until the energy of the electrons dropped below the ionization threshold. Finally, the threedimensional distribution of the ionizing events along the ion trajectory is obtained as shown in Fig. 8 for a uranium ion of 11.4 MeV/u. Due to the large number of low-energy electrons, most of the ionizations occur in a small cylinder close to the ion path, while at larger distances they result from the slowing down of energetic electrons.

In order to deduce the spatial distribution of the deposited energy, the irradiated volume of a single track was divided into cylinder shells concentrical around the ion path. The dose absorbed in each shell was calculated by integrating the energy of all ionization events in the given shell volume. The absorbed dose (i.e., the deposited energy per volume) as a function of the radial distance is displayed in Fig. 9 for vari-



FIG. 8. Ionization events along the ion trajectory (z axis) of a uranium ion (11.4 MeV/u) vs the distance from the ion path (x axis) simulated by the Monte Carlo code TRK (Ref. 48). Each dot corresponds to a single ionization event.

ous ion species of 11.4 MeV/*u*. It shows a typical $1/r^2$ dependence. We estimated that in the case of Au ions about 30% of the total energy is deposited within the SAXS radius of 1.5 nm, while the remaining 70% is available for the much larger track halo. On the abscissa of Fig. 9, we additionally marked the values of the SAXS radii by vertical lines. Comparing the experimental data with the model calculations, we find that the SAXS radius of each ion species corresponds to the same critical dose of about 2.1 ± 0.4 MGy (hatched area in Fig. 9). This value drops down to about 1.0 ± 0.2 MGy, if we use SAXS radii deduced from a track model with a radial density distribution represented by a sharp step function instead of a Gaussian curve.

IV. DISCUSSION

The results obtained independently by optical absorption spectroscopy and by SAXS indicate that the damage zone around the trajectory of an energetic ion can be characterized by a small core region with complex defect aggregates surrounded by a much larger halo consisting mainly of simple color centers. It is not possible to study both regions with the same experimental technique due to the fact that SAXS is



FIG. 9. Absorbed dose on a logarithmic scale as a function of the radial distance from the ion path (Zn, Se, Kr, Xe, Au, Pb, and U in ascending sequence). The vertical lines indicate track radii from Fig. 6 as obtained by SAXS experiments. The dose corresponding to the SAXS radius is in all cases around 2.1 ± 0.4 MGy (hatched area).

sensitive to the electron density difference between the defect aggregates and the virgin crystal while optical spectroscopy mainly detects single defects. In the fluence regime of individual (that means nonoverlapping) tracks, the concentration of larger defects is too small to be evaluated quantitatively by this technique. If we try to observe the defect clusters in the core region, extremely high fluences are needed. In such a situation, the halo regions would overlap significantly leading to a complex absorption spectrum. In such a situation, the signal of aggregated single defects in the halo cannot be separated from the defect clusters in the track core. Information exclusively related to the damage in the halo can be obtained only if overlapping of neighboring tracks is negligible, i.e., at fluences where the mean distance of the ion trajectories is larger than the diameter of the halo region. This critical fluence is, for example, about 2×10^{10} ions/cm² for Bi ions and 10^{11} ions/cm² for Zn ions.

Due to the much smaller size, the track core can be studied by SAXS at much higher fluences without reaching overlap. This technique has the advantage that for the determination of the core size, the scattering data does not depend on the ion fluence applied to the crystal. Unfortunately, we were not able to measure the absolute value of the electron density change in the tracks for three reasons: (1) the given experimental conditions did not allow us to determine the absolute magnitude of the scattered x-ray intensity, (2) the scattering intensity is a function of the square of the density change; therefore, the sign of the density change cannot be decided, and (3) the scattering intensity is a function of the number of the scattering objects; as a consequence, only a mean value can be deduced, which is averaging over the density change along each track and over all contributing tracks.

The formation of a damage strong enough to be detected by SAXS seems to be related to a critical energy loss. The same effect was found for chemical etching where tracks could be attacked only above a threshold of about 10 keV/nm. At around the same value, the SAXS contrast becomes very weak, indicating that both effects are possibly based on the same type of damage. Moreover, comparing results of the annealing experiments, both techniques seem to test defects of comparable thermal stability. Another interesting observation was made earlier,49 when LiF crystals were irradiated at low temperatures (15, 90, and 150 K). Using SAXS and chemical etching, it was found that the damage in the core region is formed almost independent of the irradiation temperature. This effect is surprising because at 15 K, the primary Frenkel defects in LiF crystals are not mobile and, therefore, cannot aggregate to larger defects.

From a combination of the SAXS results and the calculation of the lateral dose distribution, we find that the SAXS radius is correlated with the deposition of a critical dose. For various ion species, the SAXS radius corresponds to one and the same absorbed dose. This result can be interpreted as the minimum dose that is necessary to create larger defect aggregates in the track core. In the case of heavier ions, this dose is reached at a larger distance from the ion trajectory than for lighter ions. Due to the fact that the radius we deduced from the SAXS data depends on the shape of the density distribution, it is not possible to determine the critical dose with high accuracy. From annealing experiments, we conclude that the interaction of the defects in the core and in the halo of the track is rather weak for the following reason. The SAXS radii did not exhibit any notable growth at elevated temperature indicating that aggregation of a significant number of F centers from the halo to the core does not occur. Furthermore, the absorption band at 275 nm is exclusively observed under thermal treatment of samples irradiated at high fluences. We assume that such colloids are formed only in the halo region of overlapping tracks and not in the core.

The nature of the etchable damage has never been identified. However, based on the following arguments, we assume that the etchability of tracks and also the damage that causes the SAXS signal is strongly related to the formation of larger defect aggregates: (i) Gilman and Johnston demonstrated that in LiF crystals irradiated with thermal neutrons, defect clusters can be etched whereas evidence for the etchability of single defects or small aggregates (e.g., F_2 or F_3 centers) has, to our knowledge, never been found,⁶ (ii) the etchability and the SAXS pattern of tracks exhibit the same dependence under annealing, and both properties are maintained up to much higher temperatures than the survival of single defects.

If we assume that under ion irradiation, similar defect processes occur as known from conventional radiation, it can be expected that above a critical dose, defect clusters such as colloids, fluorine clusters, and vacancy clusters are formed with single defects (F centers and V centers) as precursors. As a consequence of the coagulation of F centers to larger nF aggregates, the ionic lattice collapses and metallic colloids of reduced density are formed. In this situation, the Li colloids and the molecular fluorine clusters (F_2 and nF_2) are produced with a stoichiometric ratio. Such a process requires that the F centers and the hole centers are separated in space, which normally occurs by diffusion at an increased level of the local temperature.^{5,41} Furthermore, a critical concentration of F centers of the order of 10^{19} cm⁻³ is needed. Along the path of heavy ions, this should lead to a trail of metallic colloids. Using the information we obtained about the size of the track core and the number of F centers in a single track, we can roughly estimate the number of Li atoms available for the colloid formation. For this, we have to assume that the defect creation has the same efficiency in the track core as in the halo. From the calculation of the lateral dose distribution we know that about 70% of the total energy is deposited in the halo region resulting in about 10^6 F centers per single track. About the same total number of defects (F centers or Li atoms and their complementary hole centers or fluorine molecules) should be available in the track core, although they finally agglomerate to larger aggregates. Consequently, the number of Li⁺ atoms involved should also be around 10⁶. Compared to the total number of Li ions in the cylindrical track volume (radius 1.5 nm, length 80 μ m), the number of Li atoms being available for the colloid formation reaches only a few percent. Such a small Li concentration does not allow the formation of a continuous trail of Li colloids. From this rough estimation, we expect that the track core consists of rather small defects with a distance of separation that is small enough to result in a quasicontinuous structure.

V. CONCLUSIONS

On their way through matter, energetic heavy ions deposit their energy mainly by excitation of the electron system of the target. The properties of this slowing down process is characterized by the dissipation of a considerable amount of energy in a very small volume around the ion trajectory within an extremely short time. The resulting large excitation energy density leads to a dose distribution significantly different from that caused by gamma rays or electrons that deposit the energy homogeneously in the irradiated volume leading to a uniform density of defects. In LiF crystals, the nonuniform dose distribution of energetic ions is reflected in a quite complex defect structure. Using various experimental techniques, we come to the following conclusions.

(1) Ion tracks in LiF have a structure consisting of a narrow core surrounded by a much broader halo region.

(2) The track halo consists mainly of single electron and hole centers. The radial extension of the halo increases with the atomic number and velocity of the ions and can reach several tens of nanometers. As soon as single tracks overlap, F_n centers ($n \ge 2$) and small aggregates of single defects are formed. Under annealing, single *F* centers in the halo coagulate to aggregates. The process of defect creation in the halo is similar to that under conventional radiation.

(3) New phenomena occur above a critical energy loss of around 10 keV/nm. In a core region whose diameter is about one order of magnitude smaller than that of the halo, a new type of damage is produced generating a characteristic anisotropic SAXS pattern. Moreover, it gives rise to the etchability of ion tracks, forming etch pits of the same shape as

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etched dislocations. Under thermal annealing, the etchability and the damage that cause the SAXS contrast exhibit a higher thermal stability than single defects in the halo. Both observations are correlated to a threshold of the dose deposited around the ion path.

Finally, we want to emphasize, that the damage morphology along the ion trajectories in LiF crystal owes its complex structure to several specific properties of this alkali halide, i.e., the sensitivity against electronic excitations, the rather high stability of point defects in the anionic sublattice, and the fact that the lattice of a pure ionic crystal cannot be completely amorphized.

Several questions remain open and have to be solved in the future, for instance the formation mechanism and the nature of the damage in the core, and the underlying microchemistry of the etching process. In order to clarify definitely whether or not metallic colloids are formed, various experiments are in preparation; for example, it is intended to test the resulting change of electric and magnetic properties by conductivity and electron spin resonance experiments.

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