

Ion-induced formation of colloids in LiF at 15 K

K. Schwartz,* G. Wirth, and C. Trautmann

Gesellschaft für Schwerionenforschung, Planckstrasse 1, 64291 Darmstadt, Germany

T. Steckenreiter

Technische Hochschule Darmstadt, Petersenstrasse 23, 64289 Darmstadt, Germany

(Received 10 July 1997)

LiF has been irradiated with energetic heavy ions (about 1 GeV) at temperatures between 15 and 300 K. In all cases, the ion tracks exhibited preferential chemical etching. This surprising observation gives clear evidence that the formation of etchable aggregates (Li colloids) takes place even at 15 K, although at such low temperatures all diffusion processes of primary defects are frozen. Quantitative analysis of the size of the colloids using small-angle x-ray scattering shows that the radius of the cylindrical aggregate zone is only slightly influenced by the irradiation temperature. Possible mechanisms for ion-induced colloid formation are discussed taking into account the high-excitation-energy density in the track core. [S0163-1829(97)02441-7]

In LiF and in other alkali halides, the formation and transformation of defects upon excitation of the electron subsystem has been studied for many years. It has been shown that under various types of radiation, defects are created when self-trapped excitons decay or when electrons and holes recombine. The primary Frenkel defects are F centers (an electron at an anion vacancy) and hole-interstitial H centers (a covalent halogen molecule X_2^- at a regular anion site). In LiF, F centers are stable up to a temperature of 500 K whereas the H centers thermally disappear above about 60 K. The nature and concentration of the color centers and their aggregates strongly depend on the dose, dose rate, and temperature during irradiation. At a high dose, complex microdefects (aggregation of primary F - and H centers to F_n^- and V_n centers) and macrodefects (transformation of nF centers to metallic Li colloids), covalent molecular anions (halogen molecules F_2), and vacancy clusters can be created.¹⁻³ However, in all cases where radiation induced formation of colloids was observed, the aggregation process was thermally activated either by irradiating above room temperature or by a postirradiation treatment of the samples.⁴⁻⁶ To the best of our knowledge, colloids have never been observed at low irradiation temperatures where the mobility of color centers is frozen and the aggregation process induced by diffusion is not possible. Here, we are reporting on experiments giving clear evidence that the formation of colloids in LiF becomes possible, even at irradiation temperatures as low as 15 K, if irradiated with swift heavy ions.

When irradiating LiF crystals with energetic ions, it has been demonstrated that the exciton mechanism also takes place. In a number of studies, primary defects such as F - and F_2 centers were investigated using MeV ions.⁷⁻¹⁰ More complex macrodefects were reported only in those cases where radiation was combined with thermal annealing.¹¹ In the case of GeV ions, the production of F centers and small F -center aggregates was studied along the penetration depth of the incident ions.^{10,12} In the late fifties, Young reported that in LiF single tracks of fission fragments can be revealed by chemical etching whereby the etchant attacks the damage of the ion impact zone at a higher rate than the unirradiated

crystal.¹³ More recently, we have reinvestigated this effect in more details showing that track etching is only in those cases successful where the linear energy transfer of the ions surpassed a critical threshold of about 1.2 keV/Å.^{14,15} The nature of this etchable damage has never been analyzed. However, based on the following arguments, we assume that the etchability of tracks is strongly related to the formation of defect aggregates.

(i) Gilman and Johnston demonstrated that in LiF crystals irradiated with thermal neutrons, macroscopic aggregates can be etched whereas evidence for the etchability of microdefects has never been found.¹⁶

(ii) The etchability of tracks is maintained up to a temperature of about 700 K while single defects anneal at lower temperatures.^{13,15}

(iii) Small-angle x-ray-scattering (SAXS) experiments gave a scattering pattern of high contrast only in those cases where track etching was possible.¹⁷

From the quantitative analysis of the SAXS data, it was concluded that the Li colloids are formed within the track core of a radius of 15 Å (Pb ions of 5.9 MeV per nucleon). This track core is more than one order of magnitude smaller than the outer zone (track halo) in which mainly color centers are created up to a saturation concentration.¹⁷

This knowledge of colloids in tracks of GeV ions was the base for the here described investigation. We tested if the formation of colloids using energetic ions is possible at lower temperature than required during conventional radiation. Several crystals were irradiated at different low temperatures in the range between 15 K and room temperature. The selection of the irradiation temperatures was based on the fact that specific processes mandatory for defect creation are hindered at the following temperatures:^{1,18} at 15 K, the color centers of the primary Frenkel pairs are not mobile. Therefore, the probability of F -center-interstitial-recombination is very high restricting the creation of stable defects. The efficiency to produce defects is expected to increase step by step at 90 K, where the H centers are converted into V_K centers (self-trapped holes) and at 150 K,

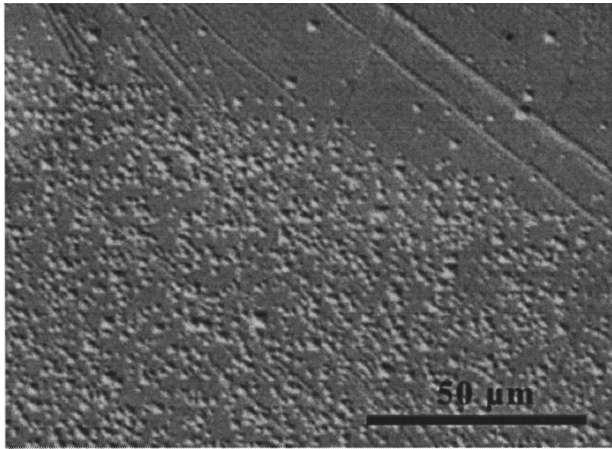


FIG. 1. Scanning electron micrograph of an etched surface of a LiF crystal irradiated through a structured mask with Pb ions (10^7 cm^{-2}) of 5.9 MeV per nucleon at $T=15 \text{ K}$. In the unirradiated region (upper right) the pyramidal etch pits correspond to dislocations.

where V_K center are not stable, and all primary H centers are transformed into more complex hole centers (V_n centers).

Thin platelets ($10 \times 10 \times 0.5 \text{ mm}^3$) were cleaved from a single-crystal block of high purity lithium fluoride grown in argon atmosphere. They were irradiated under normal incidence with ^{208}Pb ions of a specific energy of 5.9 MeV per nucleon at the linear accelerator Unilac of the GSI (Darmstadt, Germany). The fluence was 10^7 and 10^{10} ions/ cm^2 for etching and for SAXS experiments.

After irradiation, the crystals were warmed up to room temperature. It is assumed that this procedure does not influence the structure of the macroscopic aggregates, since they are stable up to a temperature of 700 K and the diffusion of the F centers takes place only above 500 K.

Chemical etching was performed in a solution of concentrated hydrofluoric acid (50 vol %) and glacial acetic acid (50 vol %) saturated with ferric fluoride.¹³ The etched surface of a sample irradiated at 15 K with 10^7 Pb ions per cm^2 is shown on a scanning electron micrograph in Fig. 1. Since the sample was irradiated through a structured grid, some areas (upper right corner of Fig. 1) were not irradiated. In this region, only etch pits of dislocations of a typical density of several 10^5 per cm^2 were found. In the irradiated area, the number of etch pits corresponded to the applied ion fluence. Etching of each single ion track resulted, as in the case of dislocations, in an etch pit of pyramidal shape owing to the cubic symmetry of the LiF lattice (Fig. 2). Track etching was observed for all tested irradiation temperatures, giving clear evidence that the formation of etchable aggregates along ion tracks takes place even at a temperature as low as 15 K. The only significant difference of the etching results concerns the mean size of the etch pits which was in the case of the irradiation at 15 K slightly smaller than that of the irradiation at room temperature. The smaller pit size indicates that the damage zone is somewhat smaller resulting in a slower growth rate at the initial stage of the etch pit formation. Chemical etching was also performed on samples which were cleaved parallel to the ion tracks (i.e., normal to the irradiated crystal surface). By etching the defects along the ion trajectory, the etchable track with a length of $40 \pm 2 \mu\text{m}$

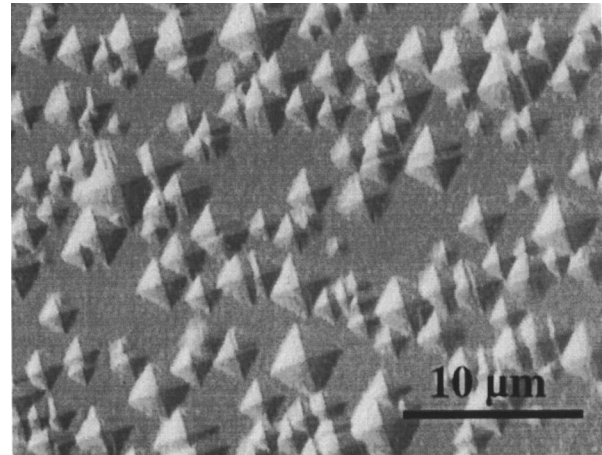


FIG. 2. Etch pits of pyramidal shape in LiF, resulting from chemical etching of ion tracks. Each pit correspond to a single ion track.

became visible (Fig. 3). According to the TRIM code,¹⁹ the projected ion range is $52 \mu\text{m}$. Taking into account the unetchable length of the ion path of about $5 \mu\text{m}$, where the energy loss drops below the critical etching threshold of $1.2 \text{ keV}/\text{\AA}$ and the etchable range, we obtain a maximum range of $45 \pm 2 \mu\text{m}$. We ascribe this discrepancy of more than 10% to a range overestimation by the TRIM code which has also been observed in various other solids.

In order to determine the size of the defect aggregates, small-angle x-ray scattering was performed on crystals irradiated with 10^{10} ions/ cm^2 . The experiments were carried out under transmission geometry with an angle of 45° between the sample surface and the x-ray beam. The rotating Cu-anode generator ($\lambda = 1.54 \text{ \AA}$) had a pinhole collimation and was operated at 49 kV and 200 mA. The ion tracks produced a characteristic scattering pattern on a position sensitive area detector. From the scattering intensity registered as a function of the scattering vector, the radius of the tracks was deduced. It was assumed that each track can mathematically be described by a continuous cylinder of a Gaussian radial density variation with the z axis of the cylinder along the ion trajectory. For such a configuration, the intensity distribution $I(k_r, k_z)$ in the reciprocal space is given by

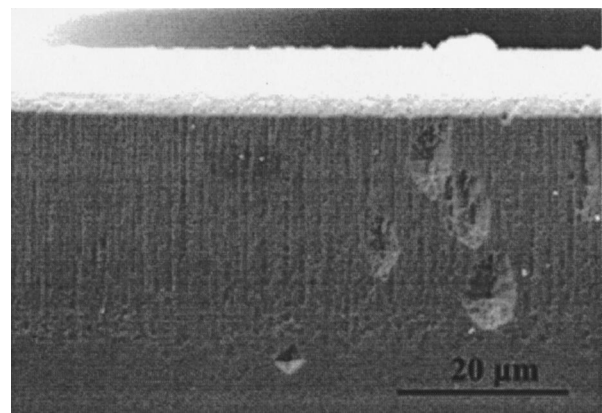


FIG. 3. Ion tracks (10^{10} cm^{-2}) in a LiF crystal (irradiation temperature 15 K) cleaved parallel to the ion beam after etching for 20 min. The length of the etched structures is $40 \mu\text{m}$ and corresponds to the ion range where etchable aggregates are created.

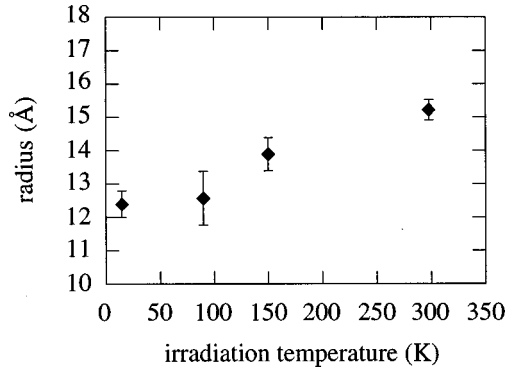


FIG. 4. Radius of ion tracks in LiF as a function of the irradiation temperature determined by small-angle x-ray scattering. The samples were irradiated with Pb ions of an energy of 5.9 MeV per nucleon and a fluence of 10^{10} ions/cm².

$$I(k_r, k_z) = \Delta\rho^2 \times 4\pi^2 \times a^4 \times \sin^2(k_z \times L) / k_z^2 \times \exp(-k_r^2 \times a^2/2), \quad (1)$$

where L is the length of the cylindrical track, k_r and k_z are the momentum vectors respectively perpendicular and parallel to the ion trajectory, $\Delta\rho$ is the maximum electron density difference between the damaged and undamaged material, and a defines the radius of the track at which $\Delta\rho$ decreases to e^{-1} .²⁰

For all tested irradiation temperatures, the crystals showed a highly anisotropic scattering pattern owing to the cylindrical geometry of the tracks. Applying Eq. (1), the radius of the ion tracks was extracted from the slope of the logarithm of the scattered intensity as a function of the scattering vector k_r . Figure 4 shows the track radii for the investigated irradiation temperatures between 15 K and room temperature. The slightly smaller track size for lower irradiation temperatures correlates with the smaller size of the etch pits obtained after chemical etching. Furthermore, the contrast of the scattering pattern was more pronounced for higher irradiation temperatures. From this observation, it can be concluded that the local electron density is smaller at lower irradiation temperatures.

The experimentally obtained radius and length of the ion track allows us to calculate the volume of the cylindrical track core in which the aggregates were created. At the irradiation temperature of 15 K, this radius is 12.4 Å corresponding to a volume of about 2×10^{-16} cm³. In such a volume, the LiF crystal contains about 10^7 pairs of Li⁺ and F⁻ ions. Assuming that all Li⁺ ions in this region are transformed into lithium colloids, the track core consists of 10^7 Li atoms in the upper limit. In reality, the concentration of Li atoms is probably smaller due to an inhomogeneous size distribution of the colloids and a density possibly smaller than for lithium as bulk material. Nevertheless, the estimated number of Li atoms in the track core is comparable with the number of single F centers (10^6 per ion track) in the track halo. This demonstrates that the efficiency for the creation of colloids in the track core is very high.

Various models have been suggested in order to describe the formation of ion tracks in insulators upon electronic

excitation.^{21–24} However, in the case of ion tracks in LiF, the creation of Li colloids, in particular the aggregation process, is still an open question. The coagulation of single F centers to F center aggregates and finally to Li colloids requires that F centers and their complementary hole centers must be separated in space and do not annihilate during the aggregation process. In LiF, both the coagulation of F centers and the separation of hole centers by thermal diffusion are impossible at $T = 15$ K. Since we did observe track etching and high contrast SAXS pattern at such a low irradiation temperature, we assume that the colloid formation results from a nonconventional process in the track core. An increase of temperature along the ion path has been postulated as a consequence of the high energy deposition.^{25,26} At the present state, reliable calculations are difficult since various processes such as the electron-phonon coupling and the transient thermal properties of the solid have to be known and effects due to radiation enhanced diffusion have to be included.²⁷ However, we will discuss two possible scenarios for the formation of colloids along highly excited ion tracks.

(a) The aggregation of point defects can take place in the solid state if diffusion and aggregation of F centers and H centers is stimulated by a local temperature increase finally leading to the creation of Li colloids and molecular fluorine (F_2 or nF_2).²⁸ The spatial separation of the F -center aggregates for the molecular nF_2 clusters must occur in the cylindrical zone of increased temperature. As a result, the Li colloids and the fluorine clusters are separated but coexisting in the track core.

(b) Due to the extremely high excitation density in the track, the situation may be described by a plasma like state consisting of free electrons and fully ionized Li and F atoms. Various fast relaxation processes take place within this plasma region without a strong interaction with the surrounding crystalline lattice which only occurs at a later stage.²⁹ The direct recombination of Li ions with free electron is dominant leading to the formation of neutral fluorine and neutral lithium atoms [the electron affinity of fluorine (3.4 eV) is smaller than the ionization energy of lithium (5.4 eV)]. At this phase, the neutral fluorine and lithium atoms are separated and F atoms rapidly diffuse out of the plasma region due to their high mobility. The driving force for such a process is possibly the different concentration of fluorine atoms inside and outside of the plasmas region. Outside of the plasma region, the neutral fluorine atoms can be transformed into molecular fluorine (F_2) or into hole centers. The Li atoms remain in the plasma region and coagulate to metallic colloids. As a result, Li colloids are mainly in the track core whereas the halogen clusters must be localized in the track halo.

Combining the observation of track etching with the quantitative analysis of the size of the track core by SAXS, first evidence was found that Li colloids can be formed at irradiation temperatures as low as 15 K. Varying between 12 and 15 Å for the 15 and 300 K irradiation, respectively, the size is extremely small and is not significantly influenced by the temperature at which the sample is kept during irradiation. It should be noted that such small colloids were never observed under conventional radiation. The small size of the colloids and the weak influence of the irradiation

temperature seem to be strongly related to the properties of energetic heavy ions. For the creation of colloids requiring a remarkable reorganization of the primary defects, energetic ions seem to be a unique type of radiation mainly for two reasons.

(a) The high amount of deposited energy results in mul-

tiplex excitation and ionization events within an extremely short time of about 10^{-15} s.

(b) The strongly inhomogeneous spatial distribution of the energy around the ion path leads to a local dose in the track core which is several orders of magnitude higher than doses typically applied by conventional radiation.

*Corresponding author. FAX: +49 6159 712179. Electronic address: K.Schwartz@gsi.de

¹N. Itoh and K. Tanimura, *J. Phys. Chem. Solids* **51**, 717 (1990).

²Noriaki Itoh and Katsumi Tanimura, *Radiat. Eff.* **98**, 269 (1986).

³P. D. Townsend, *Rep. Prog. Phys.* **50**, 501 (1987).

⁴K. Schwartz and Yu. Ekmanis, *Radiation Damage in Dielectrics* (Zinatne, Riga, 1989) (in Russian).

⁵P. Durand, Y. Farge, and M. Lambert, *J. Phys. Chem. Solids* **30**, 1353 (1969).

⁶A. Hughes and S. C. Jain, *Adv. Phys.* **28**, 717 (1979).

⁷L. H. Abu-Hassan and P. D. Townsend, *J. Phys. C* **19**, 99 (1986).

⁸A. Perez, M. Döbeli, and H. A. Synal, *Nucl. Instrum. Methods Phys. Res. B* **91**, 187 (1996).

⁹P. Thevenard, G. Guiraud, and C. H. S. Dupuy, *Radiat. Eff.* **32**, 83 (1997).

¹⁰A. Perez, J. Davenas, and C. H. S. Dupuy, *Nucl. Instrum. Methods* **132**, 219 (1976).

¹¹A. T. Davidson, J. D. Comins, A. M. J. Raphuthi, A. G. Kozakiewicz, E. J. Sendezera, and T. E. Derry, *J. Phys.: Condens. Matter* **7**, 3211 (1995).

¹²A. Perez, E. Balanzat, and J. Dural, *Phys. Rev. B* **41**, 3943 (1990).

¹³D. A. Young, *Nature (London)* **183**, 375 (1958).

¹⁴K. Schwartz, *Nucl. Instrum. Methods Phys. Res. B* **107**, 128 (1996).

¹⁵K. Schwartz, C. Trautmann, O. Geiss, and M. Krämer (unpublished).

¹⁶J. J. Gilman and W. G. Johnston, *J. Appl. Phys.* **29**, 877 (1958).

¹⁷C. Trautmann, K. Schwartz, T. Steckenreiter, and O. Geiss (unpublished).

¹⁸W. Känzig, *J. Phys. Chem. Solids* **17**, 88 (1960).

¹⁹J. F. Ziegler, P. Biersack, and U. Littmark, *The Stopping and Ranges of Ions in Solids* (Pergamon, New York, 1985).

²⁰D. Albrecht, P. Armbruster, and R. Spohr, *Appl. Phys. A* **37**, 37 (1985).

²¹R. L. Fleischer, P. B. Price, and R. M. Walker, *J. Appl. Phys.* **36**, 3645 (1965).

²²N. Itoh, *Nucl. Instrum. Methods Phys. Res. B* **116**, 33 (1996).

²³A. Meftah, F. Brisard, J. M. Costantini, E. Dooryhee, M. Hage-Ali, M. Hervieu, J. P. Stoquert, F. Studer, and M. Toulemonde, *Phys. Rev. B* **49**, 12457 (1994).

²⁴M. Toulemonde, J. M. Costantini, C. Dufour, A. Meftah, E. Paumier, and F. Studer, *Nucl. Instrum. Methods Phys. Res. B* **116**, 37 (1996).

²⁵F. Seitz and J. S. Koehler, *Solid State Phys.* **2**, 305 (1956).

²⁶M. Toulemonde, C. Dufour, and E. Paumier, *Phys. Rev. B* **46**, 14362 (1992).

²⁷Ch. B. Lushchik and A. Ch. Lushchik, *Decay of Electronic Excitations with Defect Formation in Solids* (Nauka, Moscow, 1989) (in Russian).

²⁸E. Kotomin and V. N. Kuzavkov, *Phys. Scr.* **50**, 720 (1994).

²⁹V. V. Katin, Yu. V. Martinenko, and Yu. N. Yavlinskii, *Sov. J. Tech. Phys.* **59**, 88 (1989).