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Effect of electronic energy loss and irradiation temperature on color-center creation in LiF and NaCl crystals irradiated with swift heavy ions

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LiF and NaCl crystals were irradiated at 8 K and 300 K with various light and heavy ions (C, Ti, Ni, Kr, Sm, Au, Pb, and U) of kinetic energy between about 50 and 2600 MeV, providing electronic energy losses from 0.7 to 26.4 keV/nm. A cryostat installed at the beamline allowed *in situ* absorption spectroscopy and thermostimulated luminescence (TSL) measurements from 8 K upward. Creation of electron and hole color centers is analyzed as a function of irradiation temperature, fluence, and thermal and optical bleaching. Anion interstitials (*I* and *H* centers) were only observed in crystals irradiated at 8 K. These defects are unstable and disappear in the temperature range 10–100 K. For heavy ions (Au, U), the *F*-center accumulation efficiency at low fluences is larger at 8 K than at room temperature. The opposite effect is observed for light ions (C, Ti, Ni). The results are discussed within the frame of transient heating influencing separation or annealing of point defects.

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I. INTRODUCTION

In alkali halides, the irradiation with x rays, fast electrons, and energetic ions excites the electronic subsystem of the lattice and thus can induce defects via the decay of self-trapped excitons and/or electron-hole recombination.[1,2] The primary defects are Frenkel pairs consisting of neutral (*F*-*H*) or charged ($\alpha-I$) color centers, where the *F* center is an anion vacancy (v_a^+) with a trapped electron (e^-), the interstitial *H* center is an anion (halogen) molecule (X_2^-) at a regular anion (X^-) position, the α center is a charged anion vacancy (v_a^+), and the *I* center is a negative anion ($X_{\rm int}^-$) on an interstitial position (Table I). The hole and the electron centers have to be separated by at least five interatomic distances in

TABLE I. Parameters of main color centers in NaCl and LiF crystals.:[1,2] Absorption maxima $\lambda_{\rm max}$ at indicated temperature and thermal stability up to annealing temperature T_a.

Color center	Model [a]	NaCl		LiF	
		$\lambda_{\rm max}$ (nm)	T_a (K)	$\lambda_{\rm max}$ (nm)	T_a (K)
F	$v_a^+e^-$	464 (300 K) 448 (5 K)	500	250 (300 K) 241 (5 K)	600
F'	$v_a^+2e^-$	510 (140 K)	>140	443 (5 K)	160
F_2	$2v_a^+2e^-$	720 (300 K)	500	445 (300 K)	600
$F_3(R_1)$	$3v_a^+3e^-$	544 (300 K)	500	317 (300 K)	600
$F_3(R_2)$		596 (300 K)		377 (300 K)	
$F_4(N_1)$	$4v_a^+4e^-$	825 (300 K)	415	518 (300 K)	500
$F_4(N_2)$		930 (300 K)	430	540 (300 K)	
V_3	$X_3^-=X^0X^-X^0$	~210(300 K)	500	114 (300 K)	600
H	X_2^-/X^-	330 (5 K)	80	~345(5 K)	100
H_1	H_{A1}	260 (5 K)	80		
H_2	H_{A2}	345 (5 K)	80		
V_K	$X_2^-/2X^-$	378 (80 K)	160	~345(5 K)	140
Small *F*-center aggregates	nF	563 (300 K)	~470		
Na or Li colloids (different size)	metal particle	500−700 K (300 K)	≤900	440 (300 K) 530 (300 K)	≤900
α	v_a^+	173 (5 K)		~94(5 K)	
I	$X_{\rm int}^-$	188 (5 K)	~20	~102(5 K)	~30

[a] v_a^+ is an anion vacancy; e^- is an electron; X^- is a negative charged anion; X^0 is a neutral anion; X_2^- and X_3^- are charged anion molecules; $X_{\rm int}^-$ is a charged anion on an interstitial position; H_{A1} and H_{A2} are *H* centers next to an impurity A_1 and A_2, respectively; nF is a *F*-center cluster.

TABLE II. Irradiation parameters [ion energy E, range R (Ref. 11), and mean energy loss E/R] and applied analysis technique (Sp absorption spectroscopy; TSL thermostimulated luminescence).

Ion	E (MeV)	LiF			NaCl		
		R (μm)	E/R, (keV/nm)	Analysis	R (μm)	E/R, (keV/nm)	Analysis
^{12}C	54	57.9	0.9	Sp, TSL	80.0	0.7	Sp, TSL
^{50}Ti	555	111.6	4.9	Sp, TSL	146.5	3.8	Sp, TSL
^{58}Ni	209	26.2	8.0	Sp, TSL	39.6	5.3	Sp, TSL
^{78}Kr	450	44.5	10.1	TSL	61.9	7.3	Sp, TSL
^{95}Mo	1055	90.0	11.7	Sp	120.7	8.7	
^{152}Sm	1637	98.3	17.2	Sp	135.3	12.5	Sp
	825	52.3	15.8		72.8	11.3	
^{197}Au	2187	92.6	23.6	Sp, TSL	122.4	17.9	Sp, TSL
	709	35.8	19.8		52.9	13.4	
^{208}Pb	1140	49.3	23.1	TSL	71.0	16.0	TSL
^{238}U	2640	100.0	26.4	Sp, TSL	129.4	20.4	Sp, TSL
	1400	56.8	24.6		76.2	18.4	
	900	40.9	22.0		54.9	16.4	

order to escape annihilation and to become a stable Frenkel pair.[3,4]

The observation of primary color centers requires in general low temperatures in order to restrict their mobility and thus limit defect recombination and aggregation. Charged α and I centers, for instance, transform into more stable F and H centers by tunneling processes when the temperature increases only up to 30 K for both LiF and NaCl crystals. Diffusion of H centers in NaCl (LiF) starts at temperatures larger than 80 K (100 K) leading to annihilation with F centers[5–9] and formation of more stable hole centers (V_K and V_3), as well as aggregation into X_2 anion molecules (where X_2 denotes F_2 or Cl_2 molecules).[1,2,10]

F and V_3 centers can be observed up to 500 K in NaCl and up to 600 K in LiF, indicating that their thermal stability is rather high. Diffusion of F centers leads also to formation of complex F_n centers (with $n \leq 4$), F-center aggregates (n_F), and colloids.

It should be mentioned that color centers can be also created by excitons or electron-hole pairs interacting with impurity atoms. For example, the presence of cation impurities at low temperature irradiation may trap electrons and create V_K centers (Table I).[7] Only after saturation of the impurity centers the color-center creation mechanism by Frenkel pairs (F-H and α–I) becomes dominant. Table I presents the absorption maxima and annealing temperatures of the main color centers in NaCl and LiF.

In this study, we are interested in defect creation under very high electronic excitation densities as available by irradiation with swift heavy ions of MeV–GeV kinetic energy. The energy loss of such ions along the trajectory can reach up to several tens of kiloelectronvolt per nanometer.[11,12] To investigate the response at such extreme excitations, NaCl and LiF single crystals were exposed to different ions at cryogenic (8 K) and at room temperature (RT). The analysis of the created defects was performed by means of *in-situ* optical absorption spectroscopy complemented by thermostimulated luminescence measurements (TSL), thermal annealing, optical bleaching, and scanning force microscopy. The creation of color centers and their evolution as a function of temperature were examined in a wide range of fluences. The observed effects are described with a model assuming transient track heating, which strongly influences the spatial separation of point defects in the primary Frenkel pairs.

II. EXPERIMENT

A. Crystals and ion irradiations

NaCl and LiF single crystals grown from the melt in inert atmosphere (Korth Kristalle, Germany) were cleaved along the (100) planes providing platelets ($\sim 10 \times 10$ mm^2) of thickness between 0.2 and 3 mm. These samples were irradiated at 8 and 300 K with ^{12}C, ^{50}Ti, ^{58}Ni, ^{74}Kr, ^{152}Sm, ^{197}Au, ^{208}Pb, and ^{238}U ions at the UNILAC linear accelerator of GSI (Darmstadt, Germany). The ion energy ranged from 54 to 2640 MeV with mean energy losses between 0.7 and 26.4 keV/nm (Table II). In all cases, the ion range was smaller than the thickness of the sample. The slowing down of such energetic ions is dominated by the electronic energy losses whereas contributions from nuclear stopping only plays a role close to the stopping end of the ion path. All irradiations were performed under normal incidence, applying fluences between 10^8 and 2×10^{12} ions/cm^2. To avoid sample heating, the flux was limited to 10^8 ions/s cm^2 (heavy ions) and 10^9 ions/s cm^2 (light ions). During irradiation, the ion flux was monitored with a secondary electron detector (consisting of three 1-μm-thick Al foils) placed in front of the sample and calibrated via the ion current in a Faraday cup (accuracy $\sim$20%). In several experiments, the fluence was additionally cross-checked by counting ion-

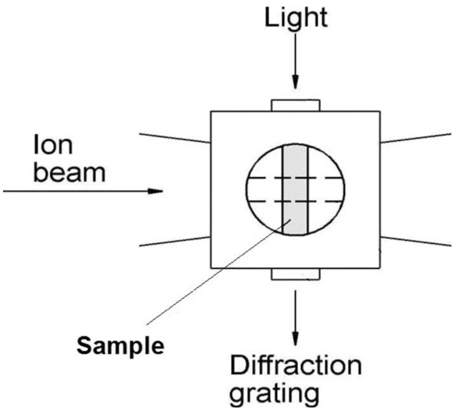

FIG. 1. Scheme of cryostat for absorption and thermostimulated luminescence measurements at the UNILAC beamline.

induced hillocks on the surface of irradiated LiF crystals.[13–15] A detailed list of the ion beam parameters is given in Table II.

The irradiation experiments at low temperature were performed in a cryostat installed at the beamline (Fig. 1). It is equipped with a compressor (COOLPAK 6000, Leybold Vacuum, Germany) suitable for operation between 6 and 300 K. The crystals were mounted on a thick copper holder using indium foils for reliable thermal contact. The sample temperature was measured with a nickel-manganin sensor (CLTS-2B, Measurement Group Inc., USA). Without beam exposure, the sample temperature was typically around 8 K, independent of the sample thickness.

B. Optical absorption and thermostimulated luminescence spectroscopy

For optical absorption measurements two different types of spectrometer were applied. Measurements at 300 K were performed off line with a double-beam spectrometer (ATI UNICAM UV4, U.K.) covering a spectral range from 190 to 900 nm and optical densities between 0.01 and 3.5. Absorption spectra from samples mounted in the cryostat were measured with an optical fiber spectrometer (DS 2000, Ocean Optics, USA) installed at the beamline (Fig. 1). The equipment allows recording spectra in the wavelength regime from 200 to 850 nm with slightly lower optical densities between 0.01 and 2.0. Spectra of samples at cryogenic temperature were recorded *in situ* during beam stops. During the irradiation, the fluence was increased in steps of typically 5×10^{8} ions/cm^2 at the initial stage and 2×10^{9} ions/cm^2 at the final irradiation stage. For NaCl, the smallest fluence leading to detectable defects was 10^{8} ions/cm^2 (for U and Au ions) and 5×10^{9} ions/cm^2 (Ti and C ions) corresponding to an optical density of 0.01.

The number of F centers produced was deduced from the optical density, D_{opt}, at the absorption maxima of the F-center band using the Smakula-Dexter formula[16–19]

$$n_F = k \times 10^{15} \times D_{\text{opt}}, \tag{1}$$

where n_F denotes the F-center concentration per unit area (cm^{-2}), and k is a coefficient which takes into account the oscillator strengths f_F of F centers. At low temperature, k must be modified due to a change of the absorption band (Table III). The mean volume concentration of F centers (N_F, cm^{-3}) is calculated by $N_F = n_F/R$, where R denotes the ion range.

TABLE III. Oscillator strength f for F-center absorption and the constant k of Eq. (1) for NaCl and LiF crystals at 300 and 8 K.

	NaCl		LiF	
f	$0.87^{c,d}$		$0.6^{a,b}$	
T	300 K	8 K	300 K	8 K
k	4.62	2.80	9.48	6.08

[a] Reference 16.
[b] Reference 17.
[c] Reference 18.
[d] Reference 19.

The determination of the concentration of the H centers is more difficult due to their smaller oscillator strength ($f_H \sim f_F/3$), larger width of the absorption peak, and overlapping of several absorption bands (H_A, V_K, etc., Table I).[2,7,20] Therefore, we only estimate the relative concentration of H centers and other hole centers based on the value of the optical density at the band maximum.

For crystals irradiated at 8 K, we also performed TSL measurements, which are more sensitive to lattice irregularities than absorption spectroscopy.[5,6] TSL thus provides additional information about those defects which are only stable at cryogenic temperatures. Applying a linear heating rate of ~4 K/min, TSL spectra were recorded up to 70 K using a photomultiplier tube (R374, Hamamatsu).

For optical bleaching, NaCl crystals ion-irradiated at 8 and 300 K were illuminated with light from a laser diode (LED 450, Ocean Optics, USA) with emission maximum at 450 nm. For NaCl, this wavelength matches the absorption band of the F centers and leads to the excitation and/or ionization of the F centers. At cryogenic temperatures the excited F centers can recombine with hole centers by tunneling processes. At higher temperatures, defect diffusion intensifies this recombination. An excited F center can also interact with other F centers or F_n centers producing more complex electron color centers (F_{n+1}) or F-center aggregates (nF).[1,2,20–24]

To study the temperature dependence of defect recombination and transformation, absorption spectra of crystals irradiated at 8 K were recorded before and after annealing to RT (heating rate ~0.5 K/min). To avoid optical bleaching, the crystals were kept in the dark during warming up.

C. Scanning force microscopy

LiF samples irradiated at 8 and 300 K were additionally examined by scanning force microscopy (SFM) using a commercial microscope (MDT Solver P47, Russia) equipped with a bar-shaped SiN$_3$ cantilever (Olympus) and a tip with a curvature radius of around 10 nm. All SFM measurements were performed in air and at RT. Topographic images were recorded in the contact mode. As known from earlier studies,[13] the impact of individual swift, heavy ions appears as nanometer-sized hillocks protruding from the sample sur-

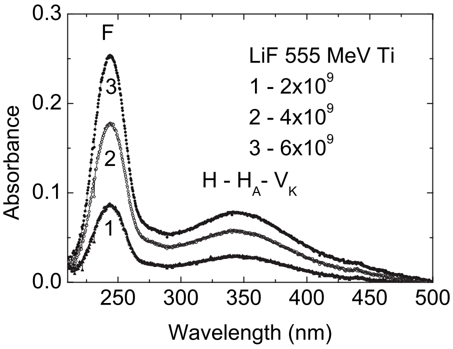

FIG. 2. Absorption spectra of LiF crystals irradiated at 8 K with Ti ions (555 MeV) of different fluence.

face. To identify a possible effect of the irradiation temperature, the diameter and height of the hillocks were analyzed from several SFM micrographs. Measurements of the number density of the hillocks served as additional fluence control.[14,15]

III. EXPERIMENTAL RESULTS

A. Effect of irradiation temperature on color-center creation

The absorption spectra of samples irradiated at 8 K are dominated by the prominent *F*-center band while the band of the F_2 centers is in general very weak. We can clearly identify several bands of hole-centers. In NaCl, the bands assigned to *H*, H_A, and V_K centers are rather well separated, whereas they strongly overlap in LiF forming a broad convoluted peak around 345 nm (Figs. 2 and 3). At 8 K, the intensity of all these bands becomes larger with increasing fluence, but the ratio of the band intensities of *F* centers to hole centers remains approximately constant (Figs. 2–4). In general, the exposure to heavier ions (U, Pb, or Au) induces a higher *F*-center concentration than light ions even if the total absorbed energy of the light ions is higher than the one for the heavy ions (Fig. 5).

Figures 6 and 7 show spectra recorded for crystals irradiated at 8 K before (curve 1) and after annealing to RT (curve 3) in comparison to crystals irradiated at RT (curve 2). Single hole centers such as *H* and H_A centers are only observable for low-temperature irradiations. NaCl crystals irradiated at 8 K and warmed up to 300 K exhibit only stable *F*, F_2, and V_3 color centers but no *H* centers. During warming up, *H* centers start to migrate and transform into V_3 centers, appearing in NaCl at around 210 nm and in LiF at 114 nm (not recorded in this study because the wavelength is out of the range of UV-VIS spectrometry). The spectra of crystals annealed to RT are qualitatively the same as those measured for samples irradiated at RT (cf. curves 2 and 3). Table IV compares the *F*-center concentration and the ratio of the *F* centers to F_2 centers of NaCl and LiF crystals irradiated with various ion beams, illustrating the effect of irradiation temperature on *F*-center creation, aggregation, and their evolution during warming up from 8 to 300 K.

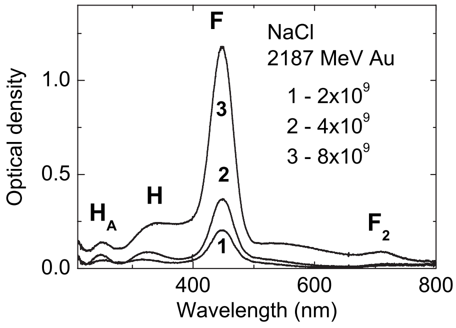

FIG. 3. Absorption spectra of NaCl crystals irradiated at 8 K with Au ions (2186 MeV) of different fluence.

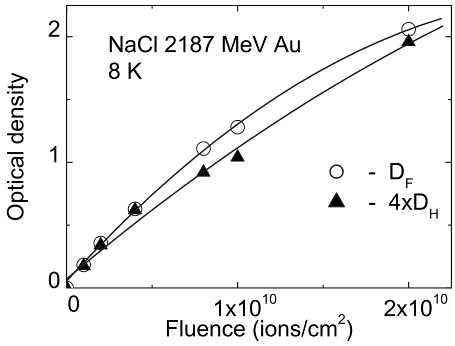

FIG. 4. Optical density as a function of fluence for *F* and *H* centers (∼330 nm) in NaCl irradiated at 8 K with Au ions (2187 MeV). In the given fluence range, the ratio of $D_H(330\ \text{nm})/D_F$ is about 0.22.

B. Concentrations of *F* centers as a function of fluence

At the initial phase of the irradiation, the *F*-center concentration grows linearly and finally saturates at large fluences (Fig. 8). This saturation behavior has been observed earlier[17] and occurs for all projectiles (at 8 K, as well as at RT) provided that the fluence applied is sufficiently high. To reach saturation with light ions requires larger fluences than with heavy ions (Fig. 8). Comparing the initial *F*-center creation rate for light and heavy ions at the different irradiation temperatures, we observe for heavy ions (Au, Pb, or U) a larger rate at 8 K than at 300 K [Figs. 8(b) and 8(d)], whereas for light ions (C, Ti) this effect is inverted [Figs.

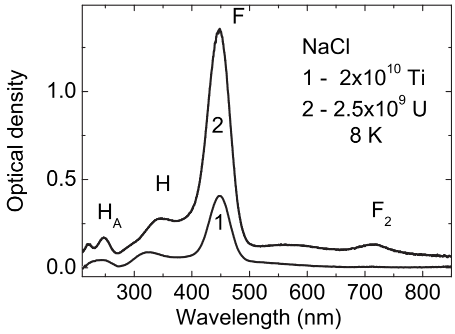

FIG. 5. Absorption spectra of NaCl crystals irradiated at 8 K with (1) Ti ions (555 MeV) and (2) U ions (2640 MeV) at different fluence corresponding to a respective energy density of 7.6 $\times 10^{20}$ eV/cm^3 and 5.1$\times 10^{20}$ eV/cm^3.

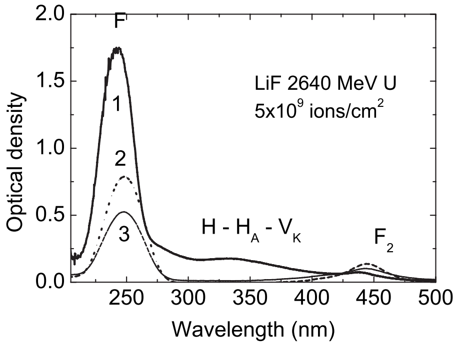

FIG. 6. Absorption spectra of LiF crystals irradiated with U ions (2640 MeV) of 5×10^9 ions/cm^2 at (1) 8 K (n_F=1.1 $\times10^{16}$ cm^{-2}), (2) 300 K (n_F=7.4×10^{15} cm^2), and (3) sample 1 annealed to 300 K (n_F=5×10^{15} cm^{-2}).

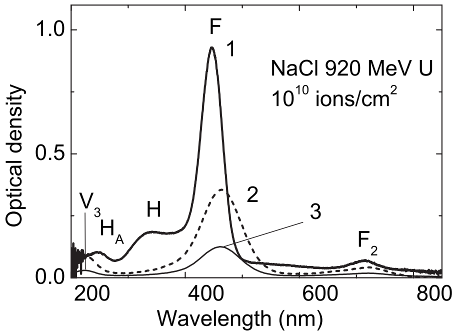

FIG. 7. Absorption spectra of NaCl crystals irradiated with U ions (920 MeV) of 10^{10} ions/cm^2 at (1) 8 K (n_F=2.5 $\times10^{15}$ cm^{-2}), (2) 300 K (n_F=1.7×10^{15} cm^2), and (3) sample 1 annealed to 300 K (n_F=6×10^{14} cm^{-2}).

8(a) and 8(c)]. This difference disappears in the case of beams of medium mass such as Sm ions (see also Table IV). We also noticed that the saturation levels of heavy and light ions at larger fluences shows a significant difference.

Figure 9 illustrates the evolution of *F* centers in NaCl for a RT exposure to Au ions up to a rather high fluence. Once complete saturation is reached, further irradiation results in a drop of the *F*-center concentration. At this point, *F* centers probably aggregate because their decrease is accompanied by an increase in the concentration of F_n centers [Fig. 9(b)]. Apart from the drop, the V_3-center concentration follows a similar fluence evolution as the *F* centers.

At low irradiation temperature, we find a correlation of the *F*- and *H*-center (X_{int}) concentrations (Fig. 4). Up to a fluence range of 2×10^{10} ions/cm^2, the ratio of their optical density remains constant (D_{opt}(330 nm)/D_{opt}(448 nm) =0.22±0.02). Concerning *F*-center aggregates, the spectra of all crystals exhibited small F_2-center bands, except for the cryogenic irradiation of NaCl with C ions and of LiF with C or Ti ions. The ratio of the F_2-to-*F*-center concentration is higher at RT than at 8 K irradiation, and heavy projectiles produce in general more F_2 centers than light ions, independent of the irradiation temperatures.

C. Bleaching of *F* centers

Bleaching of NaCl samples RT irradiated with Au ions up to a fluence 4×10^{10} ions/cm^2 in the *F* absorption band induces a considerable decrease in the concentration of V_3, *F*, and F_4 centers. Simultaneously a broad band appears ascribed to *F*-center aggregates (*nF*) and Na colloids (Fig. 10).[22,25] Analyzing the change of the absorption spectrum before and after bleaching allows us to estimate that the number of disappearing *F* centers and V_3 centers is approximately equal. Bleaching induces this pronounced aggregation only if the initial *F*-center concentration was higher than 10^{18} cm^{-3}. Bleaching at lower *F*-center concentrations leads to recombination with V_3 and to a small increase in the F_2 and F_3 center absorption.

Bleaching in NaCl irradiated at 8 K induces a decrease in the band intensities of *F* and *H* centers while the band of the F_2 centers does not change (Fig. 11). This is an indication that the *F* centers and the *H* centers at 8 K disappear mainly by annihilation rather than by aggregation.

D. Thermal annealing

For NaCl and LiF irradiated at 8 K with different ions, considerable changes of the absorption spectra occur during

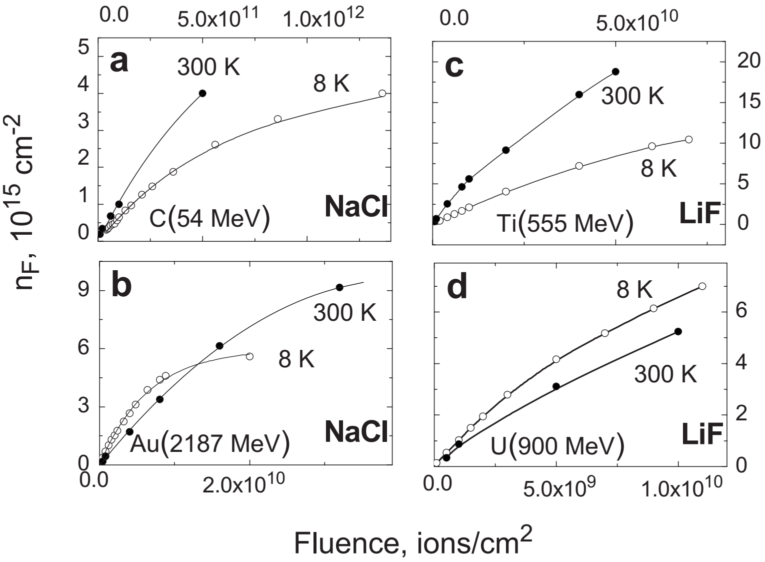

FIG. 8. Concentration of *F* centers (n_F) as a function of fluence in NaCl and LiF crystals irradiated at 8 and 300 K: (a) NaCl irradiated with 54-MeV C ions; (b) NaCl irradiated with 2187-MeV Au ions; (c) LiF irradiated with 555-MeV Ti ions; (d) LiF irradiated with 900-MeV U ions. For light ions (C, Ti) the concentration of *F* centers at 8 K is lower than at 300 K and for heavy ions (Au, U) the situation is opposite.

TABLE IV. Color-center production in NaCl and LiF crystals irradiated at 8 and 300 K: E is the ion energy, n_F is the F-center concentration, and D_F and D_{F2} denotes the respective optical densities of F and F_2 centers.

Ion	E (MeV)	NaCl $n_F(8\ \text{K})/n_F(300\ \text{K})$ Annealing Before	After	NaCl D_{F2}/D_F [a] 8 K	300 K	LiF $n_F(8\ \text{K})/n_F(300\ \text{K})$ Annealing Before	After	LiF D_{F2}/D_F [a] 8 K	300 K
^{12}C	54	0.5 ± 0.1	0.08 ± 0.02	-	0.04 ± 0.01	0.25 ± 0.1	0.10 ± 0.01	-	0.04 ± 0.01
^{50}Ti	555	0.5 ± 0.1	0.14 ± 0.03	0.03 ± 0.01	0.07 ± 0.01	0.4 ± 0.1	0.35 ± 0.04	-	0.10 ± 0.02
^{95}Mo	1055	-	-	-	-	1.0 ± 0.2	0.46 ± 0.05	0.04 ± 0.01	0.13 ± 0.03
^{152}Sm	824	1.0 ± 0.2	0.19 ± 0.04	0.07 ± 0.01	0.15 ± 0.03	-	-	-	-
^{197}Au	2187	1.6 ± 0.3	0.22 ± 0.04	0.08 ± 0.02	0.19 ± 0.04	1.0 ± 0.2	0.50 ± 0.06	0.06 ± 0.01	0.20 ± 0.04
^{238}U	900	-	-	-	-	1.4 ± 0.2	0.50 ± 0.06	0.08 ± 0.02	0.25 ± 0.05
^{238}U	2260	1.6 ± 0.3	0.22 ± 0.04	0.09 ± 0.02	0.24 ± 0.05	-	-	-	-

[a] For absorbed energy regime of about 2×10^{19} eV/cm^2 $\pm50\%$.

thermal annealing to RT. For crystals irradiated with U ions the effect is illustrated by the complete disappearance of the H-centers absorption band above 80 K (NaCl) and 100 K (LiF) (Figs. 6 and 7, and Table IV). From the simultaneous increase in the V_3-center band in NaCl, we conclude that at 300 K, about 20% of the H centers have converted into V_3 centers. We also noticed that the H_A centers disappear at higher temperatures than the H centers. This is in good agreement with earlier results for NaCl crystals irradiated with x rays at 5 K.[20]

During annealing, the F-center concentration becomes smaller; the magnitude of the decrease depends on the projectiles. The ratio of the F-center concentration at 8 K and after annealing to RT is generally larger for LiF compared to NaCl, and it scales with the electronic energy loss of the ions (Table IV). The F_2 bands also decrease significantly during annealing. The effect is more pronounced in crystals irradiated with heavy ions (Au and U) and is accompanied by an increase in the ratio of the F_2-to-F-center concentration (see Figs. 6 and 7). From the absorption change we can estimate that about 50% of the F centers in LiF annihilate by recombination with hole centers and only about 10% participate in the formation of F_2 centers.

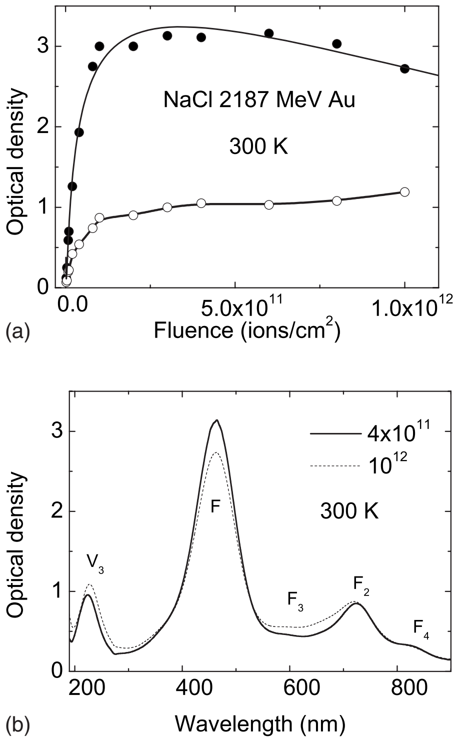

FIG. 9. Absorption data for NaCl crystals irradiated at RT with 2187-MeV Au ions: (a) Optical density of absorption band of F and V_3 centers as a function of ion fluence; (b) absorption spectra of crystals exposed to a fluence of 4×10^{11} and 10^1 ions/cm^2.

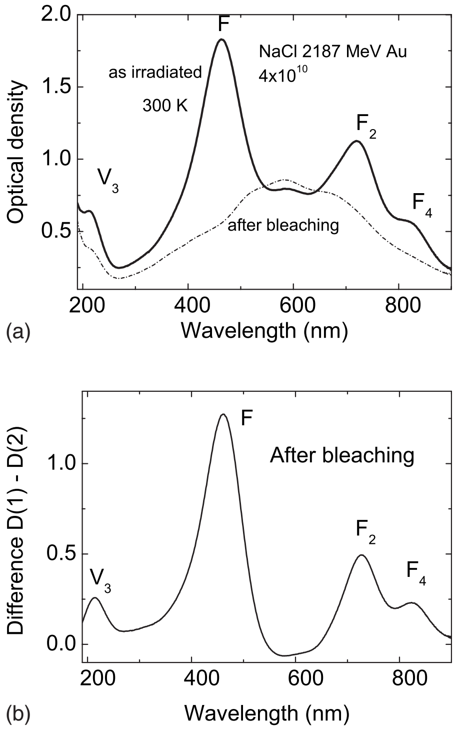

FIG. 10. Absorption spectra of NaCl crystals irradiated at 300 K with 2187-MeV Au ions of fluence 4×10^{10} ions/cm^2 (a) before (solid line) and after 30 min bleaching (dashed line) and (b) difference of spectra of (a).

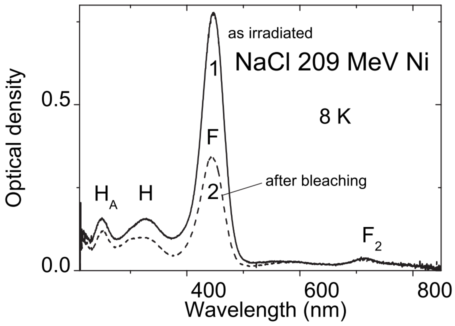

FIG. 11. Absorption spectra of NaCl crystals irradiated at 8 K with 209-MeV Ni ions of fluence 5×10^{11} ions/cm^2 as irradiated (solid line) and after 15 min bleaching (dashed line).

E. Thermostimulated luminescence

All crystals irradiated at 8 K exhibited pronounced TSL signals. The general shape of the TSL spectra was similar whatever ion species was used. Figure 12 shows typical spectra measured during warming up of samples between 8 and 70 K. For LiF, the lowest broad TSL peak appears at 12 K,[5] whereas for NaCl several peaks emerge in the range between 10 and 20 K.[6] This gives clear evidence that in both crystals, color centers are produced, which are not stable above the temperatures where the TSL peaks appear. Our TSL observations are in good agreement with earlier results from irradiations with x rays and fast electrons (Refs. 5 and 6, and references therein) assigning the TSL peaks at 10–20 K to the recombination luminescence of three complex color centers, the peaks at 26 K (NaCl) and at 29 K (LiF) to *I* centers, and the peaks appearing between 30–60 K mainly to recombination of *H* centers.

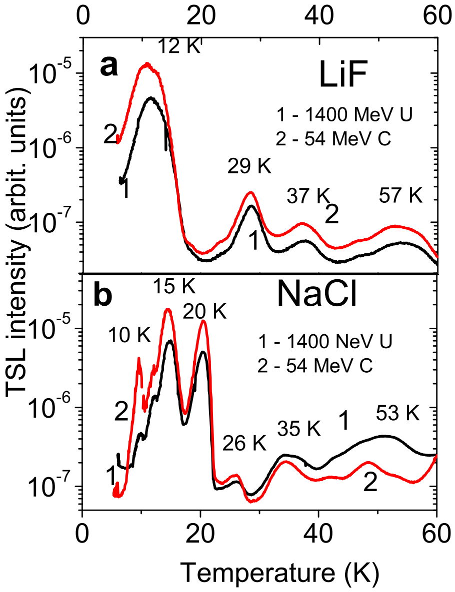

FIG. 12. (Color online) Thermostimulated luminescence of crystals irradiated at 8 K: (a) LiF exposed to 1400-MeV U ions of fluence 10^9 ions/cm^2 (1) and 54-MeV C ions of fluence 5×10^{10} ions/cm^2 (2); (b) NaCl exposed to 1400-MeV U ions of fluence 10^9 ions/cm^2 (1) and 54-MeV C ions of fluence 5×10^{10} ions/cm^2 (2).

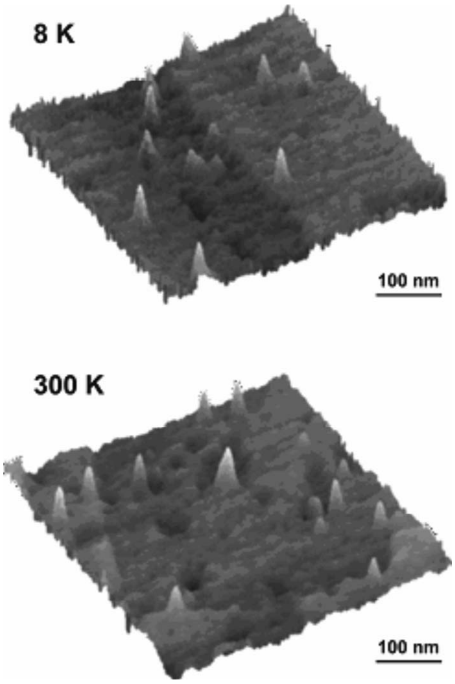

FIG. 13. Scanning force microscope image of LiF crystals irradiated at 8 K (top) and 300 K (bottom) with 1140-MeV Pb ions of fluence 5×10^9 ions/cm^2. The size of the hillocks (diameter and height) does not depend on the irradiation temperature.

In contrast to color centers, the TSL signal between 10 and 20 K TSL depends mainly on the mean energy density deposited in the irradiated sample layer ($E/R \times$ fluence) and not on the electronic energy loss of the ions. For the TSL peak at 12 K (LiF) and 15 K (NaCl), the ratio of the luminescence signal to the energy density is almost constant for irradiations with different ions up to about $\sim 10^{20}$ eV/cm^3. Above this value, the TSL emission is weaker, which can be explained by intrinsic absorption of the TSL signal by color centers.

F. Hillocks on the surface of irradiated crystals

Inspecting the irradiated surface of LiF by means of SFM, we observe nanometric hillocks (Fig. 13). Their area density coincides with the irradiation fluence, i.e., each ion impact induces a hillock. Size analysis yields a mean hillock diameter of $d(8\ \text{K}) = (19.5 \pm 3)$ nm and $d(300\ \text{K}) = (18.3 \pm 3.0)$ nm, and a height of $h(8\ \text{K}) = (0.9 \pm 0.2)$ nm and $h(300\ \text{K}) = (0.8 \pm 0.2)$ nm. There are no significant size differences for hillocks formed at 8 and at 300 K.

IV. DISCUSSION

The irradiation of alkali halides with x rays or fast electrons at liquid helium temperature decreases the efficiency of color-center creation compared to that at 300 K.[8] We observed the same temperature dependence when exposing NaCl and LiF crystals to light ions (C, Ti, Ni). In contrast to this, the efficiency of defect accumulation is larger in crystals irradiated at 8 K in comparison to that at 300 K when heavy projectiles such as Au, Pb, or U are used. As detailed in the following, we ascribe this and also other effects observed in our experiments to a transient local temperature spikes.[26,27] At elevated temperatures, the mobility of the *H* center in the genetic Frenkel pairs (*F*-*H*) becomes higher, resulting in a larger separation length and thus reducing annihilation.

The thermal energy in the lattice is provided by the electronic energy loss and via relaxation of the excited electronic subsystem in the vicinity of the projectile trajectory. The transient temperature is assumed to scale with the electronic energy loss of the ion.

The fact that our cryogenic irradiations induced *H* and *I* centers (Fig. 6, 7, and 12) that are not stable at temperatures above 80 K (NaCl) or 100 K (LiF) allows us to make a rough estimation of the local temperature. The first important fact is that the temperature increase itself, and the duration of the local thermal spike must have been long enough to separate the electron and hole center by a sufficiently large distance to avoid annihilation and form stable Frenkel pairs. Second, the maximum temperature and the duration of the thermal spike must have been sufficiently low that long-range diffusion of *H* centers is avoided (*H* centers have a much lower activation energy than *F* centers and therefore exhibit a higher mobility). This is confirmed by our observation of limited aggregation with other *H* centers, as well as annihilation with *F* centers. Once the temperature spike has elapsed, and the track region is cooled down to 8 K, the *H*-center mobility becomes negligible. The difference we find between the initial color-center concentrations at 8 K and RT irradiations is an indication of this local temperature increase.

A. Defects at low temperatures

The low temperature TSL peaks in LiF and NaCl crystals irradiated at 8 K are ascribed to various hole centers. These centers are extremely unstable and disappear when the temperature increases to 10–20 K.[5,6] The similarities of the TSL spectra for irradiations at low and at high electronic energy loss can be understood assuming that the defects responsible for the low-temperature TSL peaks are located far from the ion trajectory at a cold track periphery, where relaxation of electronic excitations is not accompanied by transient heating.

B. Effect of local temperature increase on initial color-center creation rate

The influence of the irradiation temperature on the efficiency of color-center creation at 8 K and at 300 K is reversed when comparing samples irradiated with light ions (C, Ti, or Ni) and with heavy ions (Au, Pb, or U). This difference can also be explained by temperature which influences the diffusion rate and thus the spatial separation of *H* and *F* centers. The separation length l_{HF} depends on the magnitude and duration of the local temperature increase given by $T(r,t)=T_{\mathrm{irr}}+\Delta T(r,t)$, where T_{irr} denotes the irradiation temperature, and $\Delta T(r,t)$ is the transient temperature increase as a function of time and radius. It is reasonable to assume that $\Delta T(r,t)$ is higher for heavy projectiles of large energy loss than for light projectiles. At 8 K, the transient local heating induced by heavy ions enhances diffusion in such a way that the separation between *H* and *F* centers is sufficiently large to avoid annihilation. The resulting number of stable Frenkel pairs is of the same order of magnitude as under ion irradiation at 300 K. After the thermal spike has ceased, the track region is cooled down to 8 K and the *H* centers are frozen. Their negligible mobility prevents defect recombination by diffusion and explains the increase in the *F*-center production efficiency at 8 K compared to the 300 K irradiation.

Due to the smaller electronic energy loss only negligible heating is expected in tracks of light ions. For the irradiation at 8 K, the temperature increase in the track is too low to stimulate spatial separation above five interatomic distances necessary to form stable *F* and *H* centers at 8 K. As a consequence of short separation distances, defect recombination is enhanced. This rationalizes the lower *F*-center production efficiency of light ions for irradiations at 8 K compared to 300 K. Such a behavior is similar to that described for x-ray irradiations at cryogenic temperatures.[8,20]

Short distances between complementary defects in the genetic Frenkel pairs also result in enhanced recombination of *F* and *H* centers during annealing, which explains the pronounced difference of the color-center concentration at 8 K and after warming up to 300 K. In contrast, the large initial separation of complementary color centers by heavy ions provides a chance for defect aggregation. This is evident by the larger number of surviving *F* centers [cf. ratio $n_F(300\ \mathrm{K})/n_F(8\ \mathrm{K})$, Table IV], as well as the increase in the F_2-center concentration in crystals irradiated at 8 K annealed to RT.

In order to estimate the temperature increase in the track of heavy ions, we only take into account the diffusivity of the *H* centers because they have a much higher mobility than *F* centers. The separation of *H* and *F* centers can be estimated from the *H* center diffusion length (l) during the thermal spike period as $l=(6D_H\times\tau)^{1/2}$, where τ denotes the duration of the local heating and $D_H=D_{H0}\times\exp(-U_H/kT)$ is the diffusion coefficient of *H* centers (D_{H0} is $\sim 10^{-2}\ \mathrm{cm}^2/\mathrm{s}$ and the migration energy U_H is ~ 0.03 eV).[2,5] To create a stable Frenkel pair, the separation between the *H* and *F* center should surpass at least five interatomic distances.[3,4]

Due to the nanometric size of the tracks and the short time scale of fs-ps, the temperature calculations should take into account the finite velocity of the heat front propagation as described in Refs. 26 and 27. Earlier estimations made for tracks created by 900-MeV U ions gave a thermal spike duration of $\tau\sim 10^{-11}$ s and a temperature increase in the track of $\Delta T\sim 250$ K. The diffusion length of the *H* centers is $l\approx 3-4$ nm, which is sufficiently large to separate *F* and *H* centers and thus produce stable Frenkel pairs.[3,4]

C. Saturation of *F* center concentration at large fluences

In NaCl, as well as in LiF, the saturations of the *F*-center concentration at large fluences is ascribed to a transient steady-state balance between generation of defects during irradiation and their annihilation due to both pronounced recombination of *F* and *H* centers in overlapping tracks, and aggregation of these defects into complex F_n centers and nF clusters.

For NaCl irradiated with Au ions at RT, we found clear evidence that the V_3 centers follow a similar evolution as a function of fluence as the F centers (Fig. 9), namely an initial linear increase followed by saturation. To estimate the track radius in which these defects are produced, we fitted the data by an exponential function,[28] assuming that deviation from linearity occurs as soon as neighboring tracks overlap. For the F centers and the V_3 centers we find radii of 29 ± 1 nm and 25 ± 1 nm, respectively. This illustrates that the track region in which both types of defect are created has about the same extension. Figure 9 also shows that the defect concentration at highest fluence slightly decreases for F centers whereas it still increases for V_3 centers. Although the significance of the existing data is insufficient, we may speculate that this difference is due to specific aggregation processes of F centers. During the RT irradiation of NaCl crystals, the creation of F_2, F_3, and F_4 centers is observed, indicating that the overall chance for aggregation is high. This implies that the initial separation of complementary color centers is large, providing a sufficiently high F-center concentration within the track. Such a scenario is also supported by the bleaching results, where about 50% of the F centers in NaCl are transformed into F_n- and F-center aggregates.

V. CONCLUSION

Optical absorption spectroscopy in combination with irradiation at cryogenic temperatures and subsequent annealing allowed us to study specific properties of defect creation with energetic ions characterized by high excitation levels. Primary hole centers in NaCl and LiF can only be observed under cryogenic irradiation conditions. Above, respectively, 80 and 100 K, these H centers are mobile and are known to recombine with F centers. Annihilation of H and F centers, as well as aggregation processes between homologous color centers, strongly depend on their diffusivity governed by the local temperature. As a function of irradiation temperature, the F-center creation rate for heavy ions show distinct differences compared to light ions. The effect can be explained by a local transient temperature spike, which directly influences the separation of primary H and F centers. Based on thermal spike estimations, the average temperature increase in the defect creation region is low for light ions but can reach up to 250 K for heavy ions. The transient temperature effect is also verified by annealing and bleaching experiments showing enhanced defect aggregate concentrations.

In contrast to color centers, the diameter and height of hillocks created at each ion impact sites is independent of the irradiation temperature. The mechanism of hillock formation is probably linked to stress relaxation close to the crystal surface driven by modifications produced in the core region of the tracks.

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[1] Ch. B. Lushchik, in *Physics of Radiation Effects in Crystals*, edited by R. A. Johnson and A. N. Orlov (North-Holland, Amsterdam, 1986), pp. 473–526.

[2] N. Itoh and A. M. Stoneham, *Materials Modification by Electronic Excitations* (Cambridge University Press, Cambridge, 2001).

[3] A. Ch. Lushchik and Ch. B. Lushchik, Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl.) **56**, 201 (1992).

[4] W. Meise, U. Rogulis, F. K. Koschnik, K. S. Song, and J. M. Spaeth, J. Phys.: Condens. Matter **6**, 1815 (1994).

[5] S. Nakonechnyi, T. Kärner, A. Lushchik, Ch. Lushchik, V. Babin, E. Feldbach, I. Kudryavtseva, P. Libik, L. Pung, and E. Vasil'chenko, J. Phys.: Condens. Matter **18**, 379 (2006).

[6] A. Ch. Lushchik and A. G. Frorip, Phys. Status Solidi B **161**, 525 (1990).

[7] W. Känzig, J. Phys. Chem. Solids **17**, 88 (1960).

[8] G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

[9] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[10] J. H. Crawford, Adv. Phys. **17**, 93 (1968).

[11] SRIM 2006.02 code (www.srim.org).

[12] SRIM code originally based on J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon, New York, 1985).

[13] A. Müller, R. Neumann, K. Schwartz, and C. Trautmann, Nucl. Instrum. Methods Phys. Res. B **146**, 393 (1998).

[14] M. Lang, U. A. Glasmacher, B. Moine, C. Müller, R. Neumann, and G. A. Wagner, Surf. Coat. Technol. **158-159**, 439 (2002).

[15] A. Müller, M. Cranney, A. El-Said, N. Ishikawa, A. Iwase, M. Lang, and R. Neumann, Nucl. Instrum. Methods Phys. Res. B **191**, 246 (2002).

[16] K. Schwartz, G. Wirth, C. Trautmann, and T. Steckenreiter, Phys. Rev. B **56**, 10711 (1997).

[17] K. Schwartz, C. Trautmann, A. S. El-Said, R. Neumann, M. Toulemonde, and W. Knolle, Phys. Rev. B **70**, 184104 (2004).

[18] C. J. Rauch and C. V. Heer, Phys. Rev. **105**, 914 (1957).

[19] D. L. Dexter, Phys. Rev. **96**, 615 (1954).

[20] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

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

[22] A. E. Hughes and S. C. Jain, Adv. Phys. **28**, 717 (1979).

[23] M. Enculescu, K. Schwartz, C. Trautmann, and M. Toulemonde, Nucl. Instrum. Methods Phys. Res. B **229**, 397 (2005).

[24] P. Pringsheim and P. Yuster, Phys. Rev. **78**, 293 (1950).

[25] A. T. Davidson, K. Schwartz, J. D. Comins, A. D. Kozakiewicz, M. Toulemonde, and C. Trautmann, Phys. Rev. B **66**, 214102

(2002).

[26] K. Schwartz, A. E. Volkov, K.-O. Voss, M. V. Sorokin, C. Trautmann, and R. Neumann, Nucl. Instrum. Methods Phys. Res. B **245**, 204 (2006).

[27] K. Schwartz, M. Lang, R. Neumann, M. V. Sorokin, C. Trautmann, A. E. Volkov, and K.-O. Voss, Phys. Status Solidi C **4**, 1105 (2007).

[28] P. Thevenard, G. Guiraud, C. H. S. Dupuy, and B. Delaunay, Radiat. Eff. **32**, 83 (1977).