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Defects in high-T_c superconductors after ion irradiation

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Abstract

Many irradiation experiments have been performed on high-T_c superconductors (HTS) in order to study the influence of various defect topologies on superconducting properties. In most experiments columnar defects have been generated via the electronic energy loss. While the effects of these defects on flux pinning in HTS have been studied extensively, only little has been done to understand the mechanisms by which these defects are created. Some selected experimental observations that can provide valuable insight into these mechanisms will be presented and a short description of the most successful approach to model the defect formation in HTS, the 'thermal-spike' model will be given. © 1997 Elsevier Science B.V.

1. Introduction

Superconductivity is an intriguing feature of a variety of quite different classes of materials (metals, oxides, metallic glasses and even organic compounds). It originates from a dynamic interaction between electrons (or holes) and phonons and is, thus, sensitive to details of the phonon spectrum. The latter in turn is determined by the perfection of the atomic arrangement in the lattice. The introduction of structural defects by particle irradiation generally leads to a degradation of the superconducting critical temperature T_c [1–4], while the effect of defects on the superconducting critical current density $j_c(B)$ in magnetic fields B is mostly beneficial [5–7]. Especially extended defects (i.e., with diameters of the order of the superconducting coherence length ξ) can serve as effective pinning centers for the quantized magnetic flux and thus strongly enhance the critical current density j_c [6–12]. In this case columnar defects, i.e., cylinders of amorphized material along the ion track, provide the ideal defect topology and caused the big interest in ion irradiation of high-T_c superconductors (HTS).

Two mechanisms of defect creation by energetic ions in solids can be distinguished by the way the energy of the projectile is transferred to the target atoms, namely either in elastic binary collisions (traditionally called 'nuclear energy loss', although being somewhat misleading) or, collectively first to the electrons and subsequently to the lattice ('electronic energy loss').

The defect creation due to the nuclear energy loss is completely determined by the combination of a single pair of projectile ion and target atom together with its displacement energy. This 'simplicity' allows a precise quantitative description of the radiation damage with computer codes like, for example, TRIM [13,14], even without taking into account the crystalline structure or other material dependent parameters.

Similar statements do not hold for the defect creation due to the electronic energy loss [15,16]. For this collective effect in two coupled subsystems (electrons and lattice) a profound knowledge of many material dependent input parameters is necessary in order to attempt a qualitative (or even quantitative) model description. All experiments indicate, however, that a material dependent threshold value for the electronic energy loss must be exceeded in order to create columnar defects. This threshold value is lowest for insulating materials, increases for semiconductors and is too high in most metals that it could be reached with any projectile.

The ceramic HTS exhibit features of semiconductors and metals as well. The threshold of the electronic energy loss for the creation of columnar defects is situated around $S_e \approx 10$ keV/nm in $YBa_2Cu_3O_7$ [1], a value that can easily be exceeded with ions like ^{129}Xe with an energy of several hundreds of MeV [1]. It is thus possible to perform

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extended studies of radiation damage on superconductors over the whole range of defect topologies, i.e., from isolated point defects (obtained with light ions) to highly correlated defects like columnar tracks (heavy ions). It should then be possible to gain insight into the mechanisms of the creation of columnar defects.

An old, but still most promising ansatz to describe the effects of the electronic energy loss in solids is the 'thermal-spike' model. It will be shortly described in this contribution and its predictions compared to various experimental observations.

The following sections are organized as follows: In Section 2 a selection of irradiation experiments that have been performed on HTS with emphasis on the electronic energy loss will be reviewed. The mechanisms of the creation of columnar defects will then be discussed in the framework of the 'thermal-spike' model in Section 3. Finally, in Section 4 conclusions will be drawn that demonstrate the need for further experiments and model refinements.

2. Particle irradiation of high-T_c superconductors

A brief overview of some structural peculiarities of HTS may serve as a starting point for the discussion of irradiation induced damage in this interesting class of materials. The two most widely investigated HTS are $YBa_2Cu_3O_7$ (henceforth referred to as Y123; critical superconducting temperature $T_c = 90$ K) and members of the series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (mainly with $n = 2$ and $n = 3$, Bi2212 and Bi2223; $T_c = 80$ and 110 K). From Fig. 1 the anisotropic crystal structure of these compounds is evident. Common to all HTS are the highly conducting CuO planes with insulating blocks in between. This layered structure is reflected in highly anisotropic electrical properties. The 'in-plane' resistivity along the CuO planes is found to be several orders of magnitude lower than the 'out-of plane' resistivity perpendicular to the layers. This quasi-2d electronic structure leads to an ambivalent classification of HTS as metals or insulators and has important consequences for the defect creation by electronic interactions of the projectile with the target material.

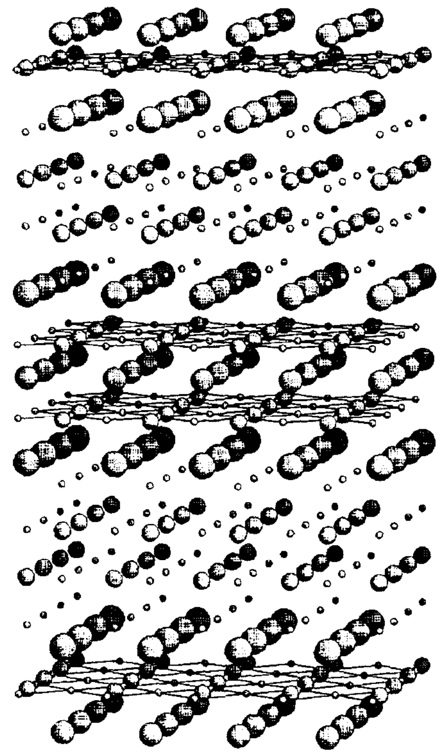


Fig. 1. The high-T_c superconductor $Bi_2Sr_2CaCu_nO_8$. Shown is a stack of 4×4 unit cells and one unit cell height. The metal atom layers are indicated, oxygen atom positions are marked by small spheres.

2.1. Irradiation with swift ions

2.1.1. Light ions

The radiation damage created by light ions in HTS, e.g., ^4He, ^{16}O with energies of several MeV to tens of MeV, can be well quantified with the classical concepts of the nuclear energy loss. In general, most experimental data like the resistivity in the normal state or the critical superconducting temperature collapse to a master-curve, when plotted against the defect concentration $\bar{V}$. The latter can be accurately calculated by available computer codes, like, for example, TRIM [13,14]. Further fine tuning can be performed by considering the real crystal structure instead of an amorphous arrangement of atoms [17]. It should be noted, however, that this refinement leads to significant differences only in some limiting cases, e.g., for single crystalline targets under channeling conditions; this is mainly due to a more correct treatment of the distribution of impact parameters. Fig. 2 shows the increase of the resistivity $\Delta\rho$ and the decrease of the superconducting critical temperature ΔT_c versus defect concentration $\bar{V}$ (expressed in dpa = displacements per atom) for Y123 irradiated with 6 MeV ^4He and 25 MeV ^{16}O [17]. The scaling of the curves to a single master-curve is evident. The linear dependence of the electrical transport properties on the defect concentration indicates a purely additive effect without further correlations between the defects, i.e., without memory. This is mainly due to the above mentioned high sensitivity of superconductors (not only Y123) to lattice defects. At the very low defect concentration (less than $\bar{V} = 0.02$ dpa) that is necessary to completely suppress superconductivity (i.e., $T_c \to 0$) no memory effects should be expected.

In comparison to other superconductors Y123 is situated between the very sensitive Chevrel-phases ($PbMo_6S_8$ [2]) and heavy-Fermion systems ($CeCuSi_2$ [3]) and the less sensitive A15-compounds (Nb_3Sn [4]). As a general rule for the HTS it can be stated that a higher degree of anisotropy means also a higher sensitivity to defects (e.g., Bi2212 is more sensitive than Y123).

2.1.2. Heavy ions

While the effects of light ions in HTS can be treated in the classical way, this is definitely not possible for heavy ions. In Fig. 3 the breakdown of the scaling to a master-curve for heavy ions is evident [17]. The resistivity enhancement $\Delta\rho$ differs by two orders of magnitude in defect concentration $\bar{V}$, while the calculation of $\bar{V}$ should be precise to better than a factor of two (irradiation and subsequent measurement of transport properties have been preformed in situ and the sample temperature never exceeded $T > 150$ K, thus annealing effects can be neglected; the ion dose was determined within $\pm 10\%$ from the electrical current that was measured on a slit assembly in front of the sample). Moreover, $\Delta\rho$ does not depend linearly on $\bar{V}$ like for light ions, but exponentially (for Kr and Xe), indicating a qualitatively different damage mechanism. Similar results have been obtained for the irradiation of Y123 with 3.5 GeV ^{129}Xe [18].

By defining a damage efficiency it is possible to compare the effects of light and heavy ions [17,19]. It can then easily be shown, that the parameter that best describes the observed qualitative differences is the electronic energy loss S_e. Below a threshold value $S_e \approx 10$ keV/nm the scaling to the defect concentration holds [1,17], while above this value the damage efficiency increases very rapidly and the scaling breaks down.

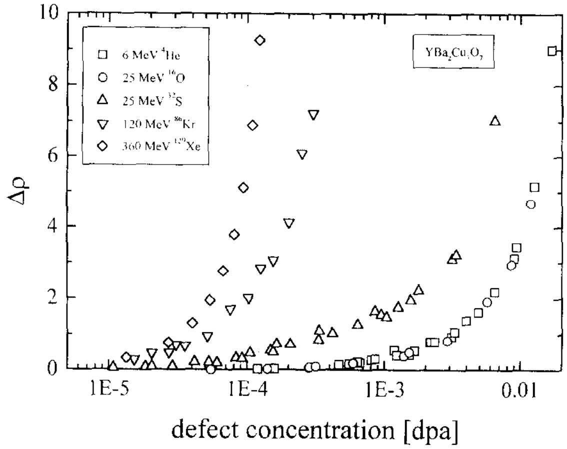


Fig. 3. Increase of the resistivity $\Delta\rho = (\rho(\bar{V}) - \rho(0))/(\rho(0))$ with defect concentration $\bar{V}$ in Y123 irradiated with 6 MeV ^{4}He, 25 MeV ^{16}O, 25 MeV ^{32}S, 120 MeV ^{86}Kr and 360 MeV ^{129}Xe. The scaling that is observed for the light ions (see also Fig. 2) breaks down for the heavy ions.

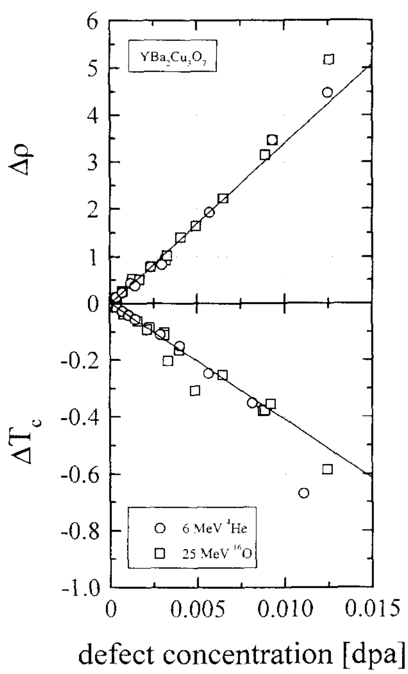


Fig. 2. Increase of the resistivity $\Delta\rho = (\rho(\bar{V}) - \rho(0))/(\rho(0))$ and decrease of the critical superconducting temperature $\Delta T_c = (T_c(\bar{V}) - T_c(0)/(T_c(0))$ with defect concentration $\bar{V}$ in Y123 irradiated with 6 MeV ^{4}He and 25 MeV ^{16}O.

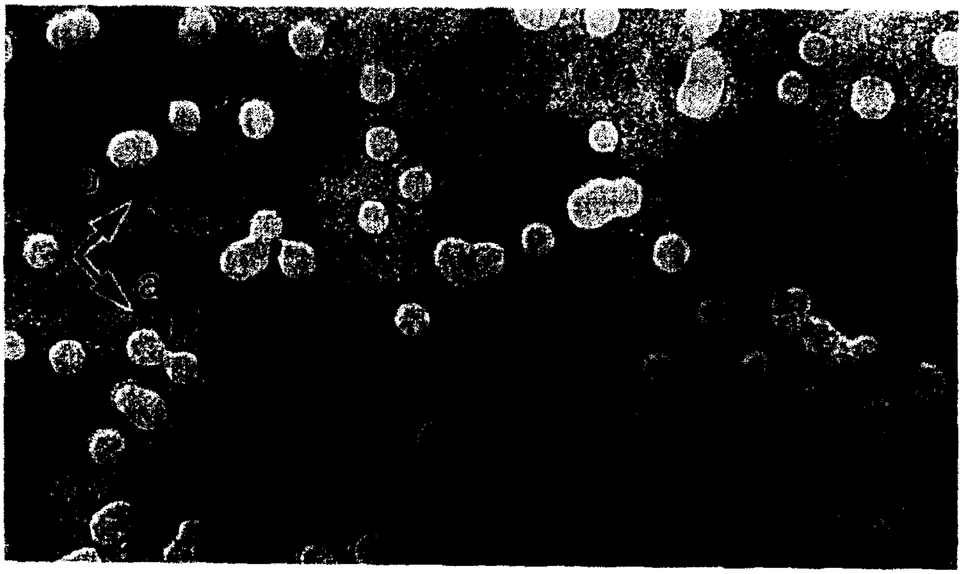
The highly increased damage efficiency of heavy ions in HTS originates from a qualitatively different type of defect that is well known from insulating materials, namely the 'latent track' (see, for example, Refs. [15,20–22]). Latent tracks are essentially cylinders of highly distorted or amorphous material along the trajectory of an incident projectile. The projectile can be an impinging ion or a fission fragment from a nuclear reaction (see Section 3). Numerous investigations have been performed to visualize the tracks in many materials by electron microscopy [7,12,18–25]. The latent tracks or columnar defects (as most of them are not 'latent' under the electron irradiation in the electron microscope) have diameters of typically $d = 2$–15 nm, depending on material and projectile. An impressive example of the visualization of columnar tracks in Bi2212 by Wiesner et al. is shown in Fig. 4 [7]. The Bi2212 films were irradiated with 10^{11} cm^{-2} 1404 MeV ^{238}U and the tracks exhibit an almost perfect cylindrical shape and a well defined interface with the matrix.

As far as the origin of the columnar defects is concerned, two models have been proposed, the 'Coulomb explosion' and the 'thermal spike'. In the scenario of the 'Coulomb explosion' a high charge density due to ionization along the projectile trajectory leads to an irreversible instability of the lattice and a resulting amorphized volume. According to the 'thermal-spike' model the energy that is deposited by the projectile leads to a strong local heating and melting of a cylindrical volume around the ion trajectory. The subsequent quench can then be too fast to permit recrystallization. What remains, is a cylinder of amorphous material. In both cases similar material properties, like thermal and electrical conductivity, play the key role in determining the stability of the material against defect formation. It is evident, that highly conducting metals with a high charge carrier density will be less affected by the deposition of even a quite high energy density, while systems like semiconductors and insulators will be very susceptible to this kind of damage. Further details of the 'thermal-spike' model can be found below.

2.2. Fission fragments

As has been shown above, it is the considerable amount of energy deposited by the projectile along its trajectory that locally destabilizes the lattice and leads to the formation of columnar tracks. It is, however, also the high electronic energy loss that is a major drawback of ion irradiation of HTS. An energy loss of 20 MeV/μm or more means that homogeneous damage can only be obtained in samples with thicknesses of several microns (or

(a)



(b)

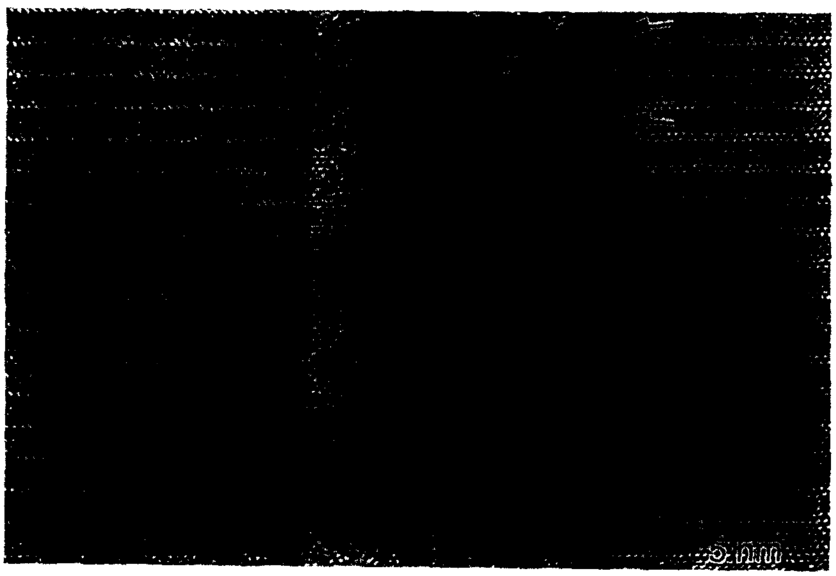


Fig. 4. Columnar tracks in Bi2212 produced by 10^{11} 1404 MeV ^{238}U. The tracks exhibit an almost perfect cylindrical shape. Shown is a plane view (a) and a cross-sectional view (b) of the columnar defects. The pictures are taken from an article by Wiesner et al. [7].

only in a thin surface layer of a bulk sample). This limitation can be overcome by 'internal irradiation'. Internal means, that the projectiles are fission fragments that are generated in the sample volume by a nuclear reaction. The primary projectiles that initiate the fission events are either neutrons or protons, that have projected ranges in solids that exceed those of heavy ions by orders of magnitude. This 'trick', however, requires doping of the material with uranium in the case of thermal neutrons or is limited to materials that contain, for example, bismuth in the case of proton irradiation. This is because only certain fission reactions produce fragments with high enough energy and mass (i.e., more precisely, charge) to exhibit a high electronic energy loss.

2.2.1. Neutrons

Only few experiments have been performed with the goal of creating columnar defects by a fission reaction that is induced with thermal neutrons [26,27]. Ceramic Y123 bulk samples have been doped with up to 380 ppm uranium and irradiated with thermal neutron fluences up to $4 \times 10^{18}/cm^2$. The main objective of these experiments was to increase the critical current density j_c in magnetic fields B by creating extended defects. Although no microscopic analyses have been published it is reasonable to assume that the fission fragments with energies $E \approx 100$ MeV created extended defects or even columnar defects via their electronic interaction. This assumption is corroborated by the observation that the undoped reference samples showed only small variations of the critical current density under neutron irradiation.

2.2.2. Protons

The above mentioned range limitation of heavy ions in HTS (and especially in silver-sheathed conductors on the basis of Bi2212 and Bi2223) was the trigger for a series of experiments in which the fission reaction is induced by protons with energies $E \approx 1$ GeV [10,11]. By transmission electron microscopy the columnar defects were visualized. In contrast to heavy ion irradiation they are not aligned, but oriented statistically ('splayed') due to the isotropic emission of the fission fragments.

For the present work monofilamentary Bi2223 silver-sheathed tapes have been irradiated with 600 MeV protons in the PIREX irradiation facility [28] at the Paul-Scherrer Institute. In two different experiments two batches of samples were irradiated with 2.5×10^{16} p/cm^2 and 10^{17} p/cm^2, roughly corresponding to 5×10^{13} and 2×10^{14} fissions/cm^3. Fig. 5 shows a transmission electron micrograph (in plane view, i.e., along the c-axis) of a grain extracted from a Bi(2223) silver-sheathed tape after irradiation with 10^{17} p/cm^2. The projections of the columnar defects can be identified in Fig. 5 by their slightly darker contrast. It should be emphasised that the tracks have a length of several microns and thus most tracks cross several of the plate-like grains.

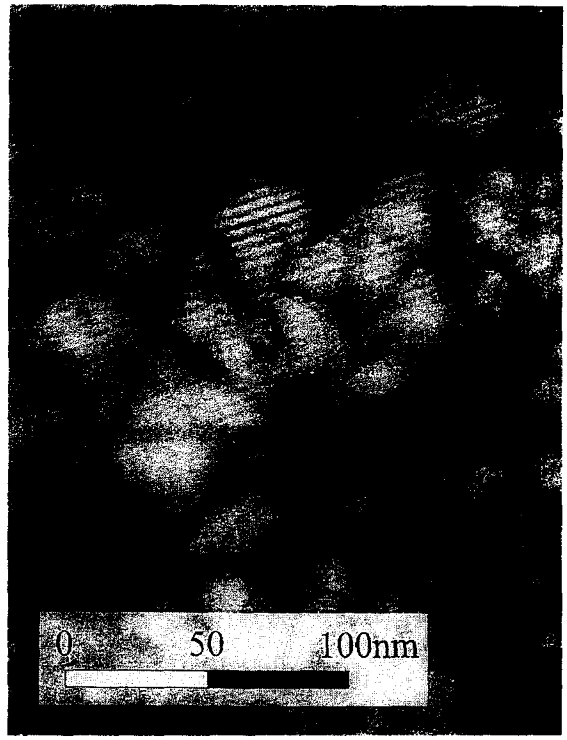


Fig. 5. Columnar tracks in Bi2223 induced by 600 MeV p [29]. The isotropic emission of the fission fragments is reflected in the random orientation of the tracks (a). The tracks are retraced in (b) in order to emphasize the distribution of track diameters (transmission electron microscopy by Paschoud).

From Fig. 5 the random orientation is evident and different track diameters can be distinguished. The variation of the diameter might originate from different fission fragments or from different relative inclinations of the fragment trajectories with respect to the c-axis. Tracks along the c-axis of HTS normally have smaller diameters than strongly inclined ones (see next Section 3).

3. The 'thermal-spike' model

The time needed for the energy transfer from the incident projectile to the electron gas of the target is much shorter than the typical time scale of lattice vibrations. The energy loss can, thus, be considered as instantaneous. The electronic excitations are then quickly converted into thermal energy of the lattice in a very localized volume around the projectile trajectory. The time scale of this secondary stage of energy transfer depends strongly on whether the target is metallic, semiconducting or ionic, in increasing order of rapidity [16]. The 'thermal-spike' model attempts to describe the spatial and temporal evolution of the local temperature from the instantaneous deposition until thermal equilibrium is reached. When during this process the melting temperature of the target material is exceeded in some volume, the formation of columnar defects should become possible.

The technical starting point for the 'thermal-spike' model is the instantaneous deposition of energy along the particle trajectory. The moment of the passage of the projectile taken as origin of the time scale it is then necessary to solve the heat equation in order to obtain the evolution of the temperature profile in the vicinity of the trajectory. It is in fact not a single heat equation that is to be solved, but two coupled equations, one for the electrons and one for the lattice. Useful approximations to this problem have been discussed in the literature [16,30].

The main result that can be obtained from such calculations is the diameter of the molten zone, i.e., a value that should directly relate to the track diameter. Considering the complexity of the problem and the necessary approximations the results are in quite good agreement with the experimentally observed diameters. The discrepancies between the predicted and measured diameters is caused by several simplifications of the model [30].

Up to now the calculations are generally limited to one dimension. This is justified as long as an isotropic target material in purely cylindrical geometry is considered. The HTS, however, exhibit extremely anisotropic properties and thus the thermal diffusivity D will depend on the direction of heat flow. This leads to an elliptical shape of tracks that are inclined with respect to the c-axis of HTS. This is understood by assuming that the deposited energy is mainly dissipated along the CuO planes. For tracks aligned with the c-axis the dissipation remains symmetric. For inclined tracks the energy transport is hindered in the direction perpendicular to the CuO planes and in agreement with this notion the tracks are observed to be elliptical. Moreover, D cannot be considered independent of temperature and will be different in solid and molten regions. The partial recrystallization that can occur after the heat pulse has also not yet been considered quantitatively in the models. A crucial test for the model, that it has not yet passed, is the description of tracks that are not continuous, but periodically modulated in diameter. These tracks, that look like 'strings of pearls' have been observed by electron microscopy [31] and still lack an explanation. They seem, however, to occur mainly when the electronic energy loss lies just above the threshold for defect creation and thus could be related to critical fluctuations.

4. Conclusions

Numerous irradiation experiments have been performed in order to create columnar defects in high-T_c superconductors. In most cases, however, the main objective was investigation of the effects of these correlated defects on flux pinning and critical current densities in magnetic fields. Detailed studies of the mechansims of the creation of these defects by the electronic energy loss S_e are rare, despite the nearly ideal conditions that the HTS offer due to their ambivalent position between metallic and insulating systems. Further experiments are necessary, especially near the threshold value of S_e for the creation of latent tracks. The thermal-spike model seems to describe the situation quite well, but still needs additional refinements to gain more accuracy.

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