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OPTICAL QUENCHING OF
PHOTOCONDUCTIVITY IN HEXAGONAL
SELENIUM SINGLE CRYSTALS

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Abstract

The photoconductivity (PC) and the quenching of PC in hexagonal Se single crystals have been studied using simultaneously two radiations with different wave lengths. Using primary radiation $E_p = 1,85$ eV, secondary radiation in the quantum energy range $1,2 \dots 1,6$ eV at 80°K always quenched the PC, but that in the range $0,7 \dots 1,2$ eV either quenched or increased the PC depending on the type of crystal. When increasing the intensity of the quenching radiation the quenching saturated at about 30% of PC. With constant weak quenching intensity the quenching in Ω^{-1} was inversely proportional to the intensity of the primary radiation. Quenching only occurs at temperatures below ca. 200°K . At least two types of centers are effective in these excitations.

Introduction

Optical quenching of PC occurs when the PC created by primary radiation is decreased by the excitations created by the quenching radiation. Usually the quenching excitations increase the recombination rate of the current carriers created by primary radiation. Optical quenching in II—VI-compounds has been studied extensively, and it has been possible to interpret the results using simple energy level models [see, e.g. Refs. 1, 2, 3]. Optical quenching in selenium has been studied very little. Both negative PC and optical quenching have been observed in amorphous Se [4], but only the optical quenching at low temperatures (during the decay of PC) in Se single crystals [5, 6]. Reasons for the scarcity of quenching investigations in Se single crystals are obvious. Effective methods for making Se single crystals have only been developed during recent years, and both the mobility mechanism and the types of centers in Se are inadequately known even when compared to those of II—VI-compounds.

TUOMI has introduced the dislocation recombination concept for the interpretation of PC in selenium [7]. This mechanism has been treated theoretically by READ [8]. According to Read's theory, there are local electron states, donors, at the dislocation cores. Some of the electrons in these centers recombine with holes causing a positive charge. To compensate this charge free holes withdraw from a cylinder around the core producing a space charge. Due to these charges, an unionized donor ex-

periences a potential U_D , which is approximately proportional to the density of ionized donors, in other words to the density of trapped holes p_I ,

$$(1) \quad U_D \approx c p_I, \quad c = \text{constant}$$

Thus the trapping parameters of dislocation centers depend essentially on this potential wall.

In normal semiconductors like Ge the density of free holes is controlled by this dislocation recombination in certain circumstances. In Se, according to thermoelectric power measurements, the density of free holes is approximately constant. Nevertheless, according to the PC-measurements [6, 7] the d.c.-conductivity σ in Se is controlled by this potential wall,

$$(2) \quad \begin{aligned} \sigma &= \sigma_1 e^{-E_B/kT} \\ E_B &= e \kappa U_D, \quad \kappa = \text{constant.} \end{aligned}$$

σ_1 is a quantity depending only weakly on temperature. Typical values of κ in Se are 0.15 to 0.2. The physical mechanism behind these relationships is not known. Tuomi proposed small angle boundaries caused by parallel dislocations, where lowest barriers E_B are a constant fraction of the potential at the core, U_D . However, when interpreting other electrical properties of Se this barrier layer concept may lead to discrepancies. Therefore, the relationships in Eqs. 2 are treated here phenomenologically as experimental facts. From Eqs. 1 and 2 we get

$$(3) \quad \sigma = \sigma_1 e^{-\beta \kappa U_D} = \sigma_1 e^{-\beta \kappa c p_I},$$

where $\beta = e/kT$.

Radiation reduces the potential walls U_D by exciting electrons to the donor states at the dislocation cores. The increase of electric conductivity, the photoconductivity, is given by

$$(4) \quad \Delta\sigma = \sigma - \sigma_0 = \sigma_1 (e^{-\beta \kappa c p_I} - e^{-\beta \kappa c p_{I_0}}),$$

where σ_0 and p_{I_0} correspond to the equilibrium and σ and p_I to the illuminated state. The trapped hole densities p_{I_0} and p_I can be calculated using the dislocation recombination theory of READ [8]. The differential equation for trapped holes, represented schematically in Fig. 1 is given by

$$(5) \quad -\frac{dp_I}{dt} = f + g - c_r e^{\beta c p_I},$$

where f is an optical excitation rate, g is a thermal excitation rate, and the recombination rate is proportional to the hole density near the dislocation, $p_0 \exp(-\beta c p_I)$. The rates f , g , and c_r depend on p_I but may be treated as constants.

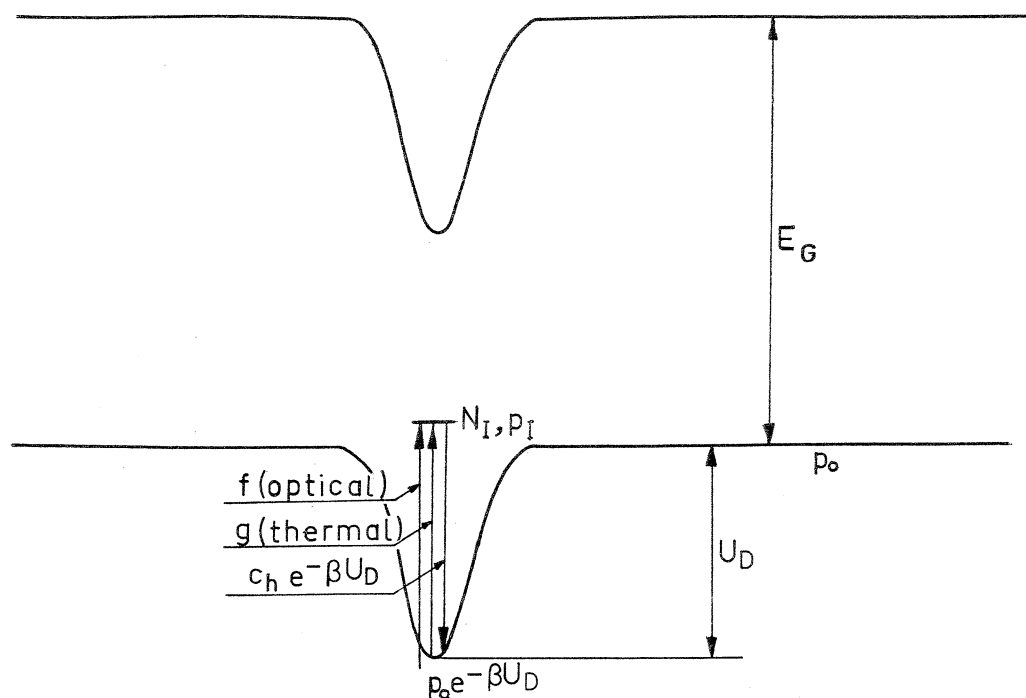


Fig. 1. Potential wall at a dislocation.

The intensity, temperature and time dependences of PC and also the thermally stimulated current have been interpreted according to this model [7]. For certain effects, however, a more complicated model is necessary. To give a quenching effect a second type of excitation must be present. Further, there are several effects in Se involving at least two types of centers. For example considering the variation of the PC when f varies stepwise. According to Eq. 5, this variation of the PC must be monotonic, but actually one observes overshooting in certain circumstances [6].

In this work the optical quenching of PC in Se single crystals has been studied both in the steady state and during the decay of PC. The results have been interpreted according to the dislocation recombination model with two types of centers.

The model

Reliable knowledge of the imperfections in the Se lattice and the corresponding electronic states of centers is very small. An additional difficulty in the case of the dislocation recombination model is that the centers at a dislocation are so close to each other that they interact. Evidently there are several types of centers, with bands rather than discrete energy levels, in the forbidden energy band. We assume that two essentially different

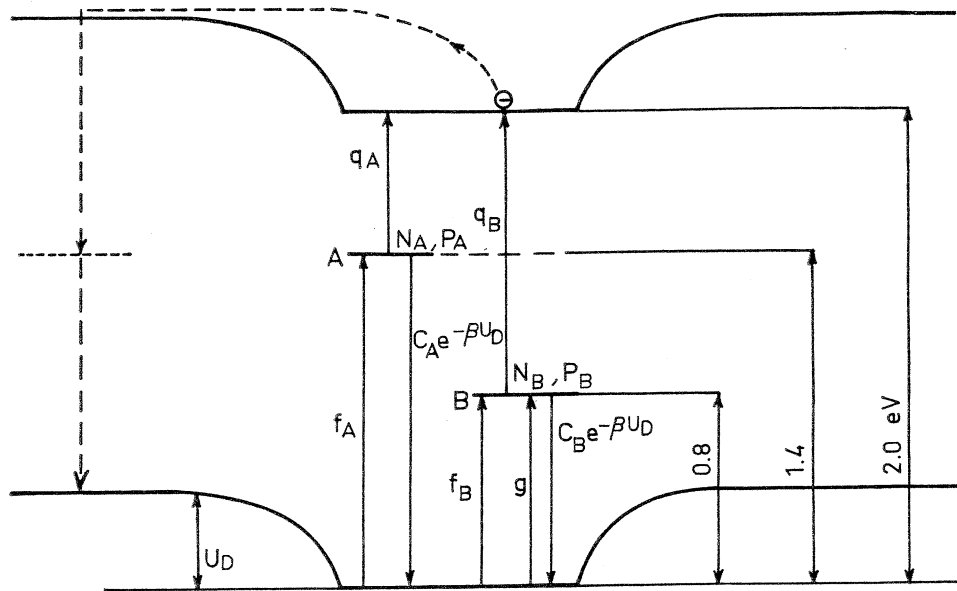


Fig. 2. PC and quenching model of Se.

types of centers A and B exist at the dislocations. The characteristic properties of these two types of centers are assumed to be determined by the properties of the Se lattice, and thus all the centers caused by different types of crystal imperfections are assumed to fall into these two categories. This gives us the model presented in Fig. 2.*)

Published data on the PC in Se can be used to determine the main features of these centers. The main PC band at 80°K starts at ca. 1,4 eV [6], so that we locate the energy level of center A at 1,4 eV above the top of the valence band. The excitation f_A is strong and is observed in all Se crystals. When the temperature rises from 80°K to 300°K this PC band shifts ca. 0,2 eV to lower quantum energies, probably because new excitations assisted by phonons become possible. The strength of the excitation f_B varies in different types of Se crystals. This excitation, starting at 0,9 eV caused a second strong PC band in deformed crystals studied by STUKE [5], and the same type of excitation can be seen as a bump in the PC spectrum at 80°K of Ref. 6. In some spectra taken in this work this excitation already begins at 0,7 eV. We locate the energy level of center B at 0,8 eV above the top of the valence band. The probability of the excitation f_B increases strongly with temperature, so that at 300°K. f_A and f_B together create a PC band beginning at 0,9 eV [6]. No PC has been

*) The nature of excitations represented is ambiguous. In addition to direct and indirect transitions excitations from a ground state to an excited state of the center or bounded exciton excitations are possible if succeeding thermal excitations result in the final state given in the figure.

reported below the quantum energy 0,7 eV (a hazy PC band at $E_v < 0,5$ eV reported in Ref. [6] has been shown to be erroneous by new measurements using a Nernst glower).

Using Eqs. 1, 3, and 5 we can write the basic equations of this barrier model with two types of centers as

$$(6) \quad \sigma = \sigma_1 e^{-\beta \kappa U_D}$$

$$(7) \quad U_D = c(p_A + p_B - N_0)$$

$$(8) \quad -dp_A/dt = f_A + g_A - q_A - c_A \exp(-\beta U_D)$$

$$(9) \quad -dp_B/dt = f_B + g_B - q_B - c_B \exp(-\beta U_D)$$

The constant N_0 depends on the type of centers (donors or acceptors). If all centers are donors, N_0 is zero. The excitations f_A and f_B decrease the barriers and produce the photoconductivity. The excitations q_A and q_B are quenching excitations. They reduce the PC provided there is a recombination process either inside or outside the space charge region which returns the electrons to the valence band. The transition rates in Eqs. 8 and 9 are proportional to the densities of states,

$$(10) \quad \begin{array}{ll} f_A \propto p_A & f_B \propto p_B \\ q_A \propto N_A - p_A & q_B \propto N_B - p_B \\ c_A \propto N_A - p_A & c_B \propto N_B - p_B. \end{array}$$

The thermal excitation rates g_A and g_B are negligible in PC studies at low temperatures. According to Read's statistics [8, 7] the total occupancy $(p_A + p_B)/(N_A + N_B)$ is something like 0.25 at 0°K in darkness.

Crystals and equipment

To study variations of the excitations in different types of crystals, four crystals obtained from different sources were used:

1) crystal H, grown from the melt at high pressure [9], length 5 mm, cross section 1×2 mm².

2) crystal S, grown very slowly from the melt [10], length 4 mm, cross section 0.7×1.0 mm².

3) crystal Cl, also grown slowly but the melt contained ca. 160 ppm chlorine, length 3.2 mm, cross section 2.2×2.0 mm².

4) crystal N, needle crystal grown from the vapour phase [11], length 5.5 mm, cross section area 0.16 mm².

Electrolytically plated nickel contacts were used for all crystals, and the electric field was in the direction of the c -axis.

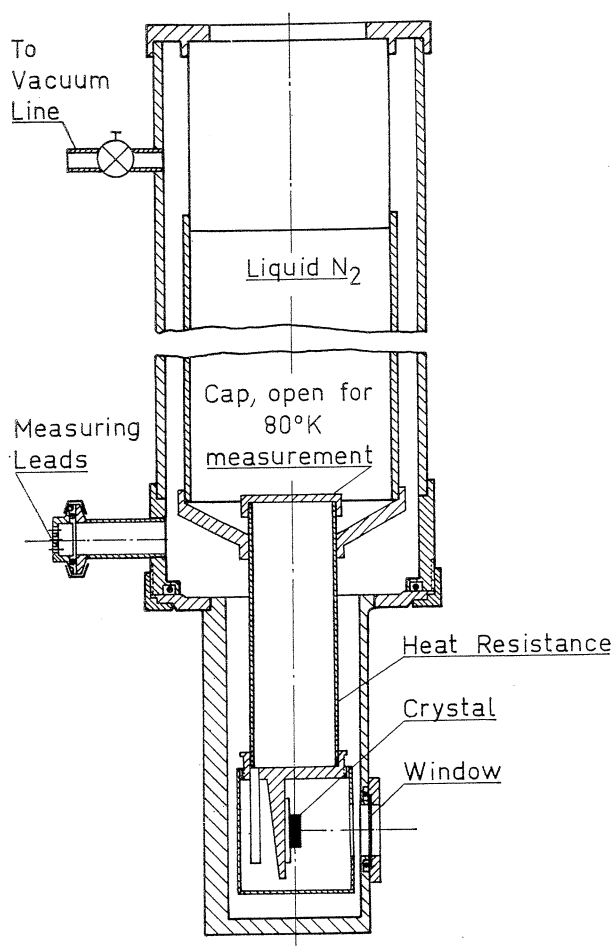


Fig. 3. Cryostat. One of the two identical windows is shown.

Steady state quenching measurements in crystals H and S were carried out at various temperatures using the cryostat shown in Fig. 3. The crystal was in vacuum. The primary radiation was filtered from the light of a small incandescent lamp. It had a quantum energy band with maximum at ca. 1.85 eV and a half width of 0.4 eV. The monochromatic quenching radiation was obtained from a Hilger-Watts monochromator. The intensities of both radiations were measured by a thermopile. When calculating quantum fluxes (intensities divided by quantum energies) a quantum energy value of 1.85 eV was used for the primary radiation. In conductance measurements a voltage of 4V was used and the current was recorded. When measuring small quenching values the primary current was compensated to achieve better accuracy. The measure used in this work for the steady state quenching is

$$(11) \quad Q = G^* - G^+,$$

where G^* is a steady state conductance with illumination by primary radiation alone and G^+ is a steady conductance with simultaneous illumination with both the primary and the quenching radiations.

The quenching during the decay of PC occurs when the slope of the decay curve of the primary PC becomes steeper during illumination with the quenching radiation. These measurements were carried out partly in the vacuum cryostat (Fig. 3) and partly in a liquid nitrogen cooled cryostat filled with argon [6].

The spectral dependence of quenching

The steady state quenching Q as a function of quantum energy in crystals H and S is shown in Fig. 4. In both crystals the quenching maxima fall between 1.4 and 1.5 eV, and at ca. 1.6 eV the quenching is compensated by excitations increasing the PC. In crystal S the quenching starts at 0.7 eV and increases steadily with increasing quantum energy, but in crystal H

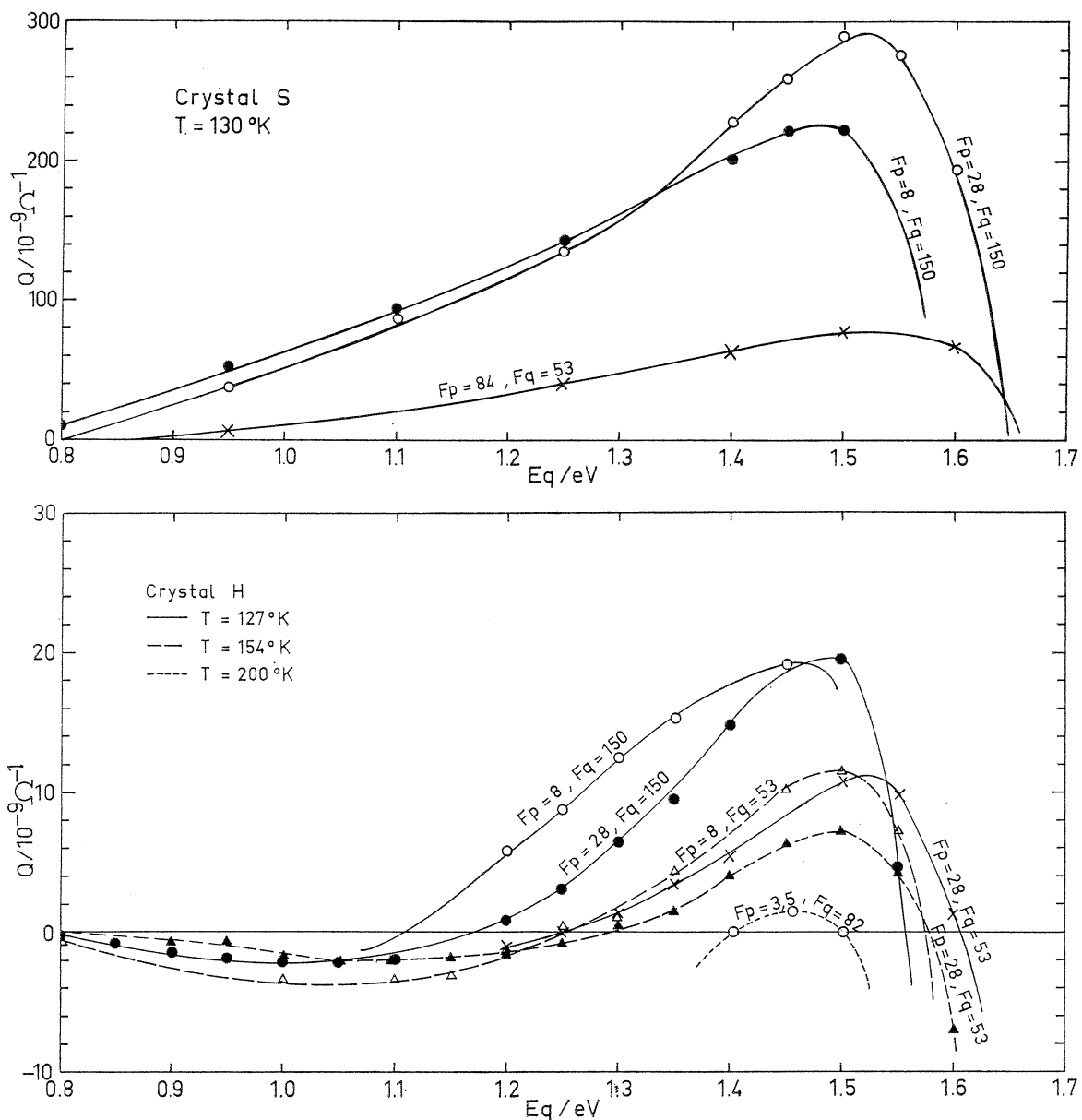


Fig. 4. Spectral dependence of quenching.

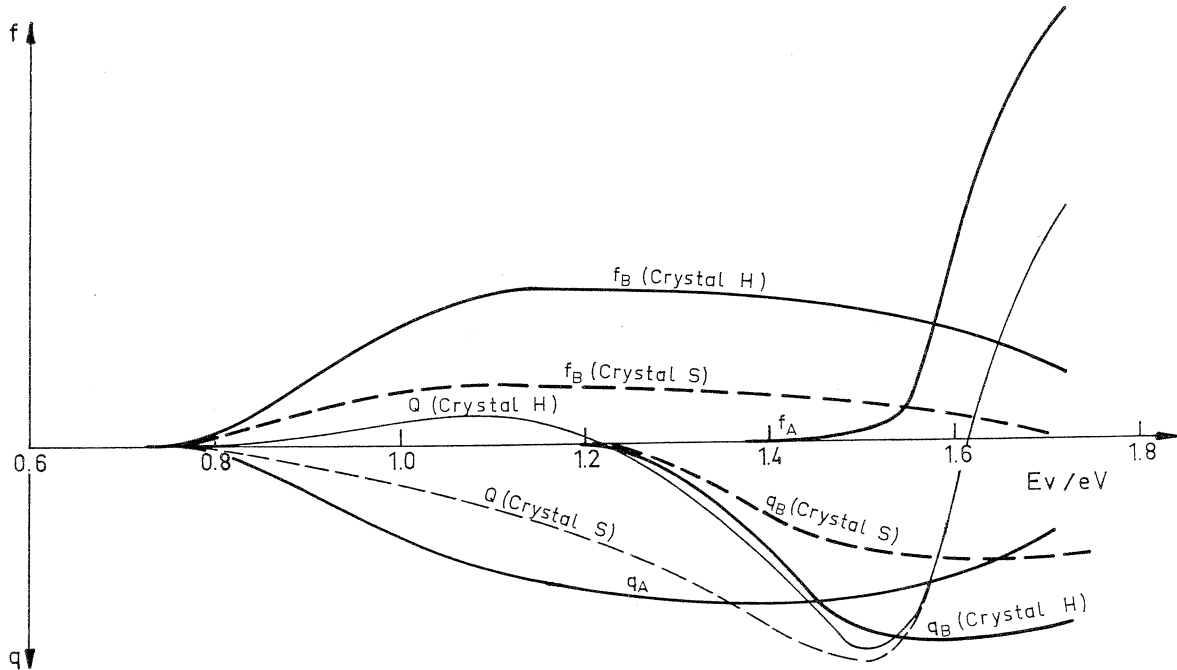


Fig. 5. Schematic spectral dependences of different excitations.

there is a band increasing the PC starting at 0.7 eV and this type of excitation changes to quenching only at 1.1 to 1.3 eV.

In Fig. 5 the excitation spectra of f_A , f_B , q_A , and q_B are sketched according to the model in Fig. 2. We see that a spectrum similar to that of crystal S can be obtained if the excitations of the center B are weak, while the spectrum of crystal H implies strong excitations of center B.

The quenching spectra determined during the decay of PC are similar to the steady state quenching spectra. In Table I a summary of the different spectra is presented and the spectra reported in earlier publications are also included.

Table I.

The spectral dependence of optical quenching in selenium

Ref.	Crystal	Experiment	Q starts	Excitation band » f_B »
this work	S	Steady St.	0.7 eV	nonexisting
[6]	S	Decay	0.75 eV	nonexisting
this work	Cl	Decay	0.9 eV	(not studied)
[5] (Stuke)	Annealed	Decay	1.0 eV	very weak
this work	H	Steady St.	1.2 eV	0.7 – 1.2 eV
this work	H	Decay	1.0 eV	0.9 – 1.0 eV
[6]	H	Decay	1.0 eV	0.8 – 0.9 eV
[5] (Stuke)	Deformed	Decay	1.35 eV	0.85 – 1.3 eV

In all experiments the quenching maximum fell between 1.45 and 1.55 eV and the quenching disappeared at 1.55 – 1.7 eV.

The temperature dependence of quenching

The temperature dependences of the steady state quenching in crystals S and H are presented in Fig. 6. When discussing the model we saw that when the temperature increases the edge of excitation f_A shifts towards smaller quantum energies and the probability of the excitation f_B increases strongly. Due to these two effects the quenching band becomes narrower and finally vanishes when the temperature increases. This becomes evident when comparing curves for different temperatures in Fig. 4.

According to Table I the excitations f_B in crystal S are weak. Accordingly, the quenching at 1.4 eV stays nearly constant up to 160°K (Fig. 6). On the other hand, in crystal H the excitations f_B are strong, and correspondingly the quenching already starts to decrease at 120°K.

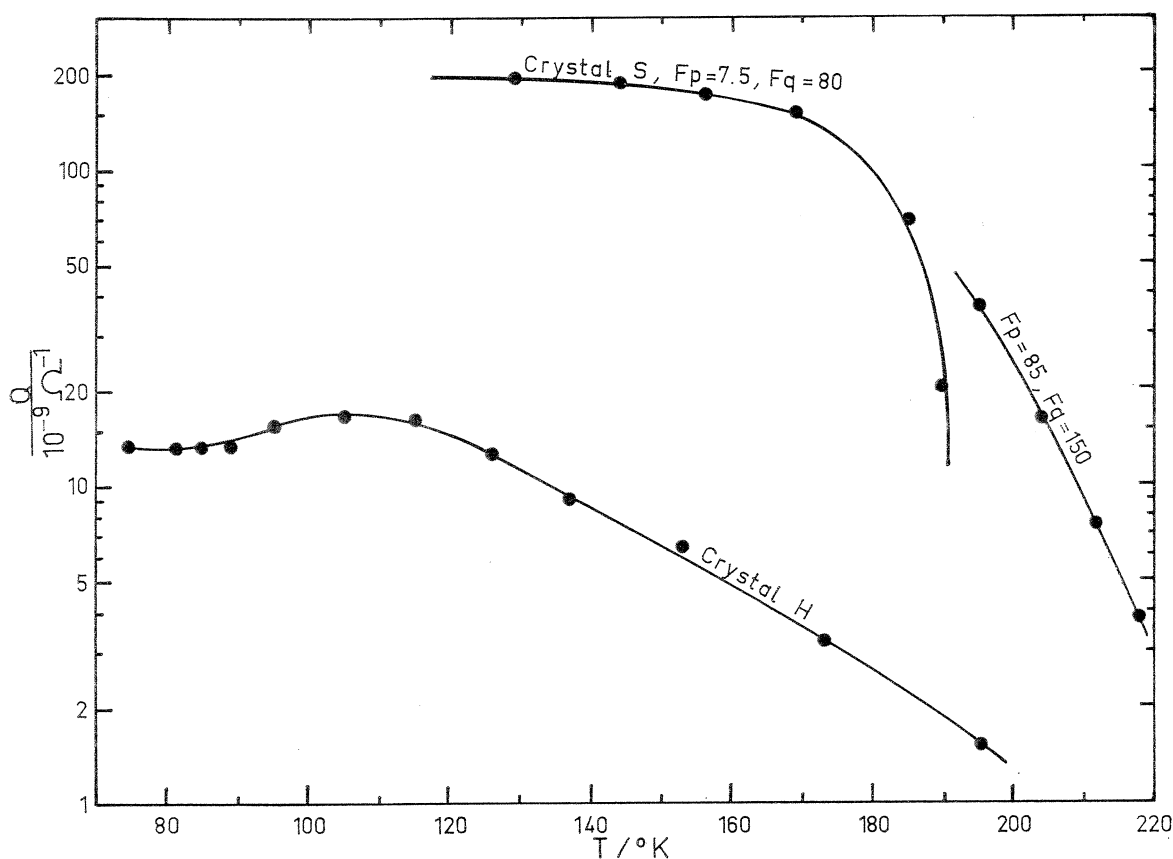


Fig. 6. Quenching vs. temperature.

Intensity dependences of quenching

In a general case the quenching radiation may excite some or all of the four excitations q_A , q_B , f_A , and f_B . Thus, according to the two center model the relationships between quenching Q and primary radiation intensity and between quenching Q and the quenching radiation intensity

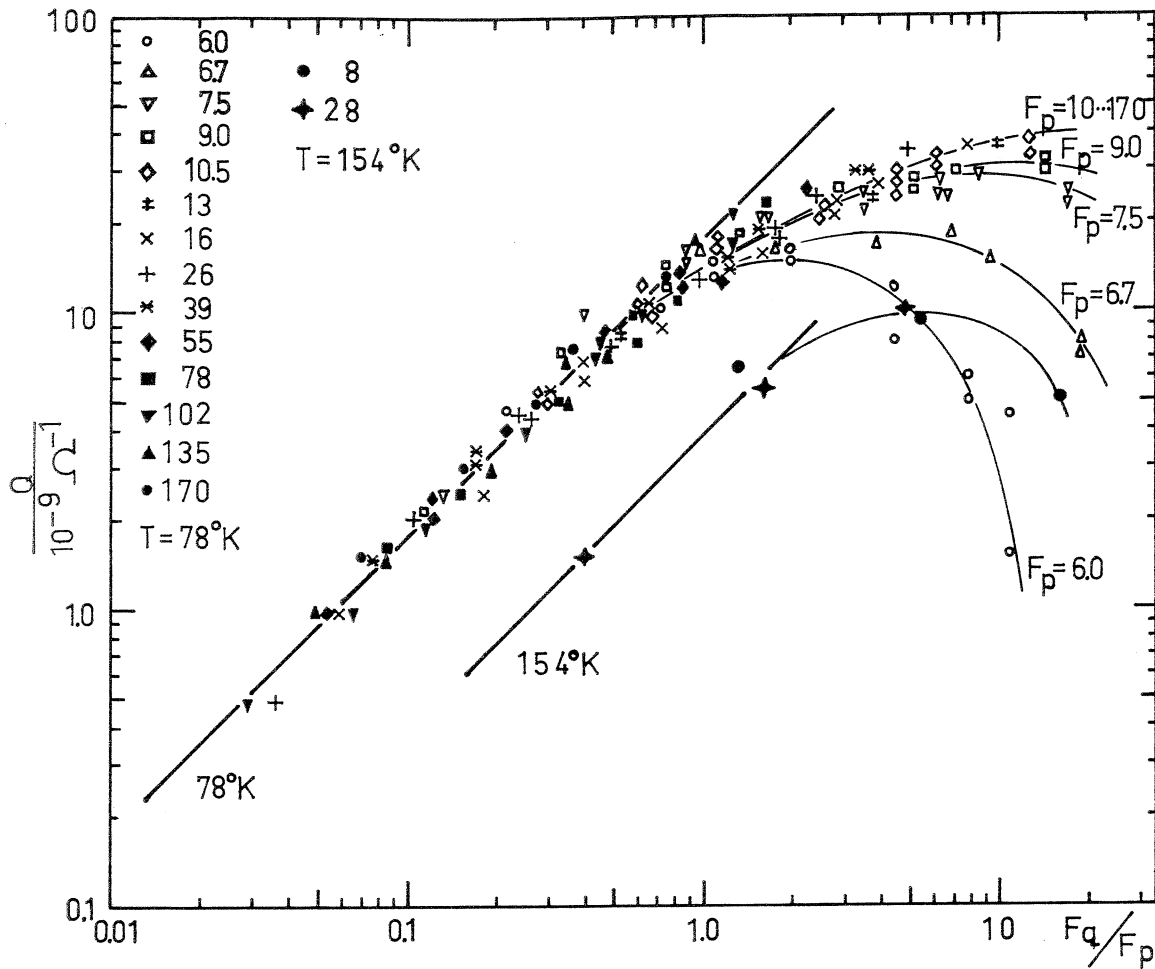


Fig. 7. Quenching vs. intensities.

depend strongly on the quantum energy of the quenching radiation, on the type of crystal and on the temperature. This is indeed the experimental situation, as one can see by comparing curves with different intensity values in Fig. 4. A more detailed experimental study of the intensity dependences was restricted to the case where the quantum energy of the quenching radiation was 1.4 eV (near the quenching maximum) and the temperature was ca. 80°K. In Fig. 7 the quenching in crystal H is presented as a function of the quantum flux ratio. We see that when the quantum flux of the quenching radiation, F_q , is lower than that of the primary radiation, F_p , the quenching is given by

$$(12) \quad Q = Q_0 \frac{F_q}{F_p}, \quad Q_0 = \text{const.}$$

When the quantum flux of the quenching radiation becomes larger than that of the primary radiation the function $Q(F_q)$ either saturates or starts to decrease.

The *weak quenching* can easily be calculated according to the model. Let us assume that the height of the potential barriers is essentially determined by centers A. Both primary quantum flux F_p and quenching quantum flux F_q excite f_A and q_A simultaneously,

$$(13) \quad \begin{aligned} f_A &= k_{fp} F_p + k_{fq} F_q, \\ q_A &= k_{qp} F_p + k_{qq} F_q. \end{aligned}$$

However, the primary radiation excites mainly f_A , and thus the constant k_{fp} is larger than k_{qp} . The quenching radiation excites mainly q_A , so that the constant k_{qq} is larger than k_{fq} . When the primary radiation alone is used, according to Eq. 8 we get

$$(14) \quad \exp(-\beta U_D^*) = (k_{fp} - k_{qp}) F_p / c_A,$$

and when both radiations are used we get

$$(15) \quad \exp(-\beta U_D^+) = [(k_{fp} - k_{qp}) F_p - (k_{qq} - k_{fq}) F_q] / c_A.$$

According to Eqs. 11 and 6 we get for the quenching

$$(16) \quad Q = G^* (1 - G^+ / G^*) = G^* \left(1 - \frac{\exp(-\beta U_D^+)}{\exp(-\beta U^*)} \right).$$

By using Eqs. 14 and 15 this equation becomes

$$(17) \quad Q = G^* [1 - (1 - KF_q / F_p)^\kappa], \quad K = \frac{k_{qq} - k_{fq}}{k_{fp} - k_{qp}}.$$

In the quenching range $Q/G^* = 1.5 - 12\%$ this function can be replaced, with accuracy better than 5%, by a function

$$(18) \quad Q = G^* \bar{\kappa} (KF_q / F_p)^{(1+\kappa)},$$

where $\bar{\kappa}$ is a constant a little larger than κ . The intensity dependence of PC in selenium is [6]

$$(19) \quad G^* = \bar{G} F_p^\kappa, \quad \bar{G} = \text{const.}$$

Thus, *the small quenching as a function of the two intensities is*

$$(20) \quad Q = Q_0 \frac{F_q^{1+\kappa}}{F_p}, \quad Q_0 = \bar{G} \bar{\kappa} K^{1+\kappa}.$$

Thus, in agreement with the experimental results Q is inversely proportional to F_p . In this calculation we omitted the effects of the excitations f_B and q_B (Eq. 9) and the effects of the variations of rates f_A , q_A , and c_A caused by the variation in the occupation of center A (Eqs. 10). These effects cause the saturation of $Q(F_q)$ or even the decrease of Q when

increasing F_q at small F_p -values, in agreement with the experimental results (Fig. 7). Obviously, for the same reason the exponent of F_q in Eq. 12 is a little smaller than that in Eq. 20.

The same intensity dependences of small quenching (Eq. 12) were observed at temperatures 80°K, 127°K, and 154°K in crystal H, and also in crystal S. As mentioned earlier, these detailed intensity measurements were carried out using the quenching quantum energy 1.4 eV only.

Three characteristic properties of the quenching in Se are:

a) The largest absolute quenching, saturation value Q_0 , occurs in Se single crystals when the primary quantum flux is large enough and the quenching quantum flux is 2 to 10 times the primary quantum flux.

b) The largest quenching in percentage of PC, Q/G^* , was about 30% in every crystal. This quenching occurred when the primary radiation intensity chosen created a PC about three times the saturation quenching Q_0 mentioned in Eq. 12, and when F_q was roughly ten times F_p .

c) Two series of conductance values in crystal H at 80°K using different quenching radiation intensities:

	1)	2)
primary radiation 1.85 eV alone	45 nS	45 nS
quenching radiation 1.40 eV alone	37.5 nS	70 nS
both radiations together	41 nS	70.5 nS

In the first case the quenching is only 10% of the primary PC, but the conductance created by both radiations together is smaller than the average of the conductances created by each radiation alone. In the second case the quenching as defined by Eq. 11 does not exist. However, the quenching radiation masks the photoconductance of the primary radiation almost completely.

Time dependences of quenching

Time dependences of quenching in hexagonal Se are very slow, as are also the time dependences of PC in Se. Quenching vs. time curves are roughly exponential at small primary and quenching radiation intensities, but become strongly nonexponential if one or both of the intensities are large.

Let us define the rise time of quenching as the time needed for quenching to reach a value of 63 per cent of its steady state value Q and the decay time of quenching as the time needed for the quenching to decrease to a value of 37 per cent of its steady state value. The rise time decreases when increasing either the primary radiation intensity or the quenching radiation

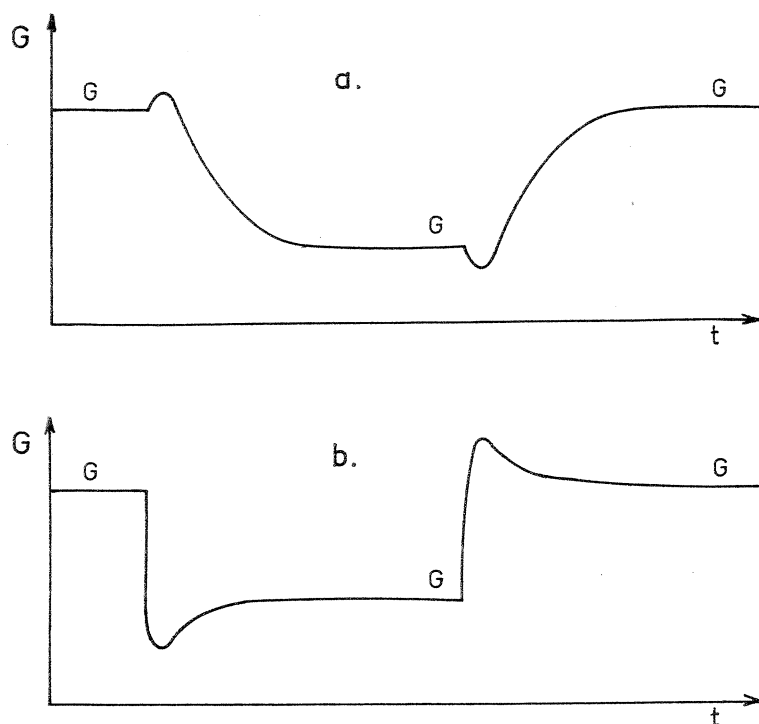


Fig. 8 a, b. Time transients of quenching.

intensity. The decay time does not depend appreciable on the quenching radiation intensity but decreases when increasing primary radiation intensity. Usually the decay time is longer than the rise time but the two become nearly equal at high intensities. At liquid nitrogen temperatures the rise times observed varied in the range 3 min to 0.8 sec and the decay times observed varied in the range 7 min to 0.8 sec. When the temperature was increased the rise and decay times decreased rapidly. Thus, the effects of intensity and temperature on the time dependences of quenching and photoconductivity are similar.

At quenching radiation quantum energies *larger than 1.5 eV* fast transients of the type shown in Fig. 8a occurred in every crystal studied. Similar transients have earlier been observed when the quenching during the decay of PC has been studied [6]. To explain these transients a two center model is necessary. According to the model presented in Figs. 2 and 5 these transients occur when the fast excitation f_A causes an increase of PC and a subsequent slow excitation q_B causes a stronger quenching.

In crystal H reverse transients (Fig. 8b) occurred when the quantum energy of the quenching radiation was in the range 1.2 to 1.3 eV and the ratio F_q/F_p was about 2.5. According to Fig. 5 this quenching is mainly caused by excitation q_A , and a simultaneous PC-excitation in this case is f_B . The transient occurs when the excitation q_A is fast and the excitation f_B is slow.

Quenching during the decay of photoconductivity

An experimental arrangement for measurements of quenching during the decay of PC is simpler than that for steady state measurements. The earlier quenching results in Se single crystals reported in Refs. [5] and [6] were obtained during the decay of PC. As mentioned earlier, the spectral dependence of quenching in decay measurement is similar to that in steady state measurement (Table I), and the same holds for the temperature dependence of quenching. The time transient of the type shown in Fig. 8a also occurred in every crystal. A typical quantity in these decay measurements is the slope ratio. One measures the slope of the decay curve immediately before and immediately after quenching is initiated. The inverse ratio of these slopes describes the increase of recombination caused by the quenching radiation. The largest measured value of this ratio was 25 in crystal S, 20 in crystal Cl, and 12 in crystals H and N. The dependence of this slope ratio on the quantum energy of the quenching radiation is similar to the spectral dependence of steady state quenching. From the few measurements carried out the intensity dependences of this ratio are qualitatively similar to the intensity dependences of steady state quenching. This kind of result is also expected from the model.

Conclusion

The quenching in Se, measured in Ω^{-1} , was inversely proportional to the intensity of the primary radiation, when constant weak quenching light intensity was used. This exceptional dependence is connected to the unusual photoconductivity and mobility mechanisms of Se.

In every Se single crystal studied the radiation in the quantum energy range from 0.7 eV to the band gap (about 2 eV) caused excitations which affected the electrical conductivity. The detailed nature of these excitations is not known. Clearly, they are caused by crystal imperfections, because the absorption coefficient in the small absorption range varies widely in different specimens. These crystal imperfections are associated with dislocations, as

- a lattice deformation creating dislocations simultaneously creates a new PC band and causes a quenching band to disappear [5],
- a thin Se crystal is transparent in red light, but this transparency vanishes when the crystal is deformed [12],
- heat treatment changes the absorption coefficient of Se [13] analogously to the effects of deformation and heat treatment on the electrical conductivity and PC in Se [5],

— furthermore, the PC cannot be explained on the usual PC models but can be explained by excitations and recombinations in dislocation centers [7].

No sharp lines or narrow bands exist in the spectral dependences of absorption, PC, or quenching in Se, according to Refs. [13, 14, 6] and Fig. 4 in this work. Therefore, the excitations from the ground state with discrete energy level to the excited state with discrete energy level are excluded. In Ref. [13] it is suggested that a continuous broad band of energy states lies in the forbidden energy band. In this work the spectral dependences of excitations in Fig. 5 are interpreted as excitations from various states of the valence band to centers with discrete energy levels and excitations from these centers to various states in the conduction band.

The excitations either increase electrical conductivity (PC-excitations) or decrease the conductivity (quenching excitations). *Any light in the quantum energy range 0.7 eV to 1.8 eV simultaneously creates at least one type of PC-excitation and one type of quenching excitation in selenium.* Therefore the dependences of optical quenching on the quantum energies and intensities of the primary and quenching radiation as well as the time dependences of quenching are quite complicated functions. However, the diversity of the experimental results in PC and quenching studies can be interpreted, at least qualitatively, according to a model with two types of centers at the dislocation cores. In this model all the different types of excitations are grouped into the PC- and quenching excitations of centers A and B situating in the barrier regions (Fig. 2).

Apart from quenching, three other effects have been reported in crystal S [6], which can readily be explained on the basis of fast A-centers and slow B-centers:

1) After strong illumination at 80°K with 1.85 eV light and short time interval in darkness, weaker 1.85 eV light caused a transient represented in Fig. 9a.

2) At 300°K when illuminated with 1.7 eV light the initial rise curve is slower than that after illumination followed by a short interval in darkness (Fig. 9b).

3) In some circumstances an overshoot was observed at 80°K in the PC rise.

In Fig. 9 the occupations of centers A and B have been sketched for qualitative explanation of these effects. Of course simple addition is not correct, but rather one should use Eqs. 6—10.

The excitation f_A is strong in every Se single crystal. Therefore, the type A center must always be present in the potential barrier regions of Se crystal. On the other hand, as seen in Table I the excitation band f_B varies strongly in different types of Se crystals and thus the density of centers B

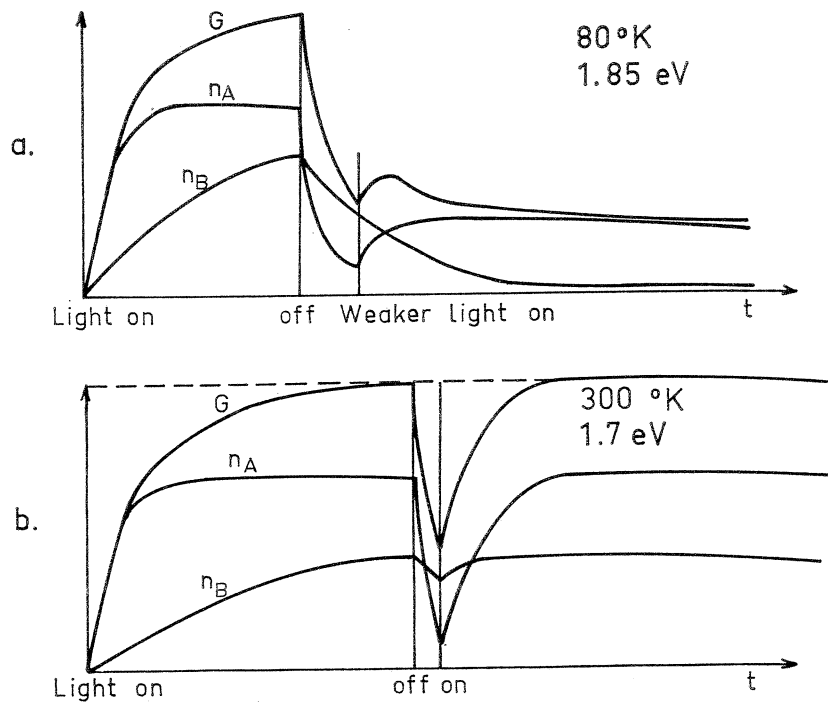


Fig. 9 a, b. Time transients of photoconductivity.

vary strongly from crystal to crystal. Type B centers also seem to be created during deformation and can be to some extent removed by heat treatment [5, 13]. We may classify Se single crystals as either »weak B» with a low density of centers B or »strong B» with a high density of centers B. Referring to Table I we see that crystals S and Cl then belong to the »weak B» group and crystals H and N to the »strong B» group.

The main difference between these groups naturally occurs in the spectral dependences of PC and quenching. However, several further differences of these groups could be explained according to the model. First let us consider a temperature dependence of PC in a strong illumination case. In the limit of no B-centers the PC is, according to Eqs. 6 and 8

$$(21) \quad \sigma^*(T) = \sigma_1 \left(\frac{f_A - q_A}{c_A} \right)^{\alpha} = \text{const} \cdot \sigma_1(T)$$

Thus the temperature dependence of PC is determined by $\sigma_1(T)$ and this temperature dependence is weak. On the other hand, in the »strong B» crystals if one removes the holes p_A nearly completely there are still barriers cp_B (Eq. 7) and the PC is

$$(22) \quad \sigma^*(T) = \sigma_1 \exp(-\kappa ecp_B/kT).$$

Therefore, the PC may be expected to decrease with temperature. (An excess light ca. 1 eV exciting f_B does not help because it also causes a

quenching q_A). Experimental PC data of the crystals studied seem to support this idea. When the temperature was reduced from 300°K to 80°K the PC of »weak B» crystal S doubled but the PC of »strong B» crystals H and N decreased to values a third and a tenth of that at room temperature, respectively.

After the initial rise the thermally stimulated current (TSC) vs. temperature in Se is similar to the temperature dependence of PC [7]. Therefore a definite difference can be expected in the TSC curves of »weak B» and »strong B» crystals. Indeed, in »weak B» crystals S and Cl the TSC decreased strongly after the initial rise, but in »strong B» crystals H and N it stayed nearly constant.

A third difference between these groups is in the slope ratio of the decay quenching curve. According to the sketch in Fig. 5 the 1.4 eV quenching in »weak B» crystals should be more effective than that in »strong B» crystals. As mentioned above, the largest ratio observed in »weak B» crystals S and Cl was about twice as large as that in »strong B» crystals H and N.

The density of centers B can be reduced by heat treatment, as mentioned above. A similar reaction occurs more slowly even at room temperature. After decay quenching measurements of »strong B» crystal N two years ago this crystal has changed considerably towards »weak B» type. In crystal H this evolution was stronger: half a year after the measurements reported here the excess excitation band shown in Fig. 4 had vanished.

Two types of centers (donors and traps) have already been suggested by Stuke in the interpretation of his experimental results [5]. The measurements presented here give a qualitative idea of the location of the energy levels A and B, the excitation spectra, and the recombination parameters of the model. By using a computer one could determine the model parameters quantitatively by fitting the experimental curves with those obtained from the Eqs. 6 to 10. However, as the model presented here is basically phenomenological, and includes too many unknown parameters this fitting would not give much additional information.

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