

<https://doi.org/10.3176/phys.math.1970.3.09>

S. MURADOV,* M. ELANGO

ON THE ROLE OF MOBILE HOLES, ANION VACANCIES AND EXCITONS IN THE IRRADIATION-INDUCED COLOURATION OF KCl CRYSTALS

The radiative production of F-centres in KCl, KCl(Ag), KCl(Pb) and KCl(H) and B-centres in KCl(Ag) as well as the radiative destruction of B-centres in KCl (Ca, Ag) and reproduction of U-centres by the optical bleaching of F-centres in preliminarily irradiated KCl(H) have been studied at temperatures between 80 and 400°K. The processes connected with the migration of holes (the 2nd stage of F-centre production), anion vacancies (B-centre production, optical $F \rightarrow U$ conversion) and excitons (the 1st stage of F-centre production, radiative B-centre destruction) have been found out. The temperatures for delocalization of holes (205°K), anion vacancies (235°K) and excitons (250°K) in KCl crystals have been determined.

1. Introduction

The mobility of electron excitations and structure defects is of a great importance in the processes of radiative production of colour centres in alkali halide crystals. At present, it is generally accepted (see e.g. the survey papers [1-3]) that, at low temperatures, colour centres arise mainly as a result of the decay of relaxed excitons (X_2^*). The primary defects — α -centres (anion vacancies v_a^+), F-centres ($v_a^+e^-$) and their complementary centres, i. e. I-centres (interstitial halide ions X_1^-) and H-centres (interstitial halide atoms X_1^0), which are produced in this way, have a very low mobility near LHeT. "Hot" X_1^- and X_1^0 are able to migrate over a distance of several lattice parameters from their production places, which keeps the "centre — complementary centre" system off the immediate monomolecular annihilation. The firm localization of X_1^- and X_1^0 after their thermalization keeps arising centres off the bimolecular annihilation and leads to a comparatively high defect production yield in alkali halides at low temperatures (e. g., in KCl one F-centre is produced per 1200 eV of absorbed energy at LHeT [4]).

The gradual rise of crystal temperature changes the situation because the complementary centres become movable even being in the thermalized state. This leads to the decrease of the defect production yield due to bimolecular recombinations of centres and complementary centres. In KCl this occurs at temperatures about 20°K (recombinations of I-centres and α -centres) and 50°K (recombinations of H-centres and F-centres) [5]. As a result of those recombinations, the defect production

* Permanent address: Institute of Nuclear Physics, Uzbek SSR Academy of Sciences, Tashkent, USSR.

yield in KCl is several times lower at LNT in comparison with that at LHeT [5]. Its decreasing to zero is hindered evidently by the interaction of moving defects with impurities and localized defects (e. g., with V_K -centres [6]).

If the raise of the irradiation temperature is continued, holes (V_K -centres), excitons and vacancies become mobile. That leads to further complications in the colouration process due to the partial destruction of centres already produced, on the one hand, and to the appearance of new effective mechanisms of colouration, on the other. Finally, at temperatures 400–600°K the motion of vacancies reaches such an intensity that all the centres will be destroyed immediately after their production [7].

In this paper, new and generalized literature data are presented which permit to clarify the role of the motion of holes, anion vacancies and excitons in the processes leading to the radiative production of some electron excess colour centres in pure and impurity-doped KCl crystals.

2. Experimental Procedure

The production and decay of colour centres have been studied by following the growth and decrease of corresponding bands in absorption spectra of crystals with an automatically operating spectrophotometric equipment and spectrophotometer SF-4. Samples were coloured in a liquid nitrogen cryostate by exposing them to x-rays from a tungsten target of the tube BSV2 (55 kvp, 18 mA, filtered by 1.2 mm of aluminium). Growth curves for colour centres have been improved, taking account of the temperature dependence of the height and half-width of the corresponding band.

The nominally pure and Ag-, Pb- and H-doped KCl crystals grown in this laboratory in air atmosphere by the Kyropulos method and cleaved to yield 1.0 ± 0.1 -mm-thick samples have been used in experiments. The concentration of Ag- and Pb-impurities in doped samples has been about 0.1 and 1.0 mol% (in the melt), respectively. Samples were doped with H-impurity by the usual procedure [8].

3. Results

The growth curves for the number of F-centres in KCl, KCl(Ag), KCl(Pb) and KCl(H) have been registered during 3 hours at various temperatures between 80 and 400°K and decomposed into elementary stages by plotting them (after extrapolating their linear part to $t = 0$) in the semilog-scale. After this treatment it turned out that a typical growth curve consists of three stages, two of them saturating with the irradiation time (during about 15 and 100 min respectively) as a function like

$$n_i = n_i^\infty (1 - \exp(-\alpha_i t)),$$

n_i being the number of centres produced to time t , n_i^∞ — the saturating value of n_i , α_i — the rate constant of the i -th stage ($i = 1, 2$). The third stage has a constant rate (dn_3/dt) in our dose interval*.

* Analogical stages in the colouration of NaCl have been stated in paper [9].

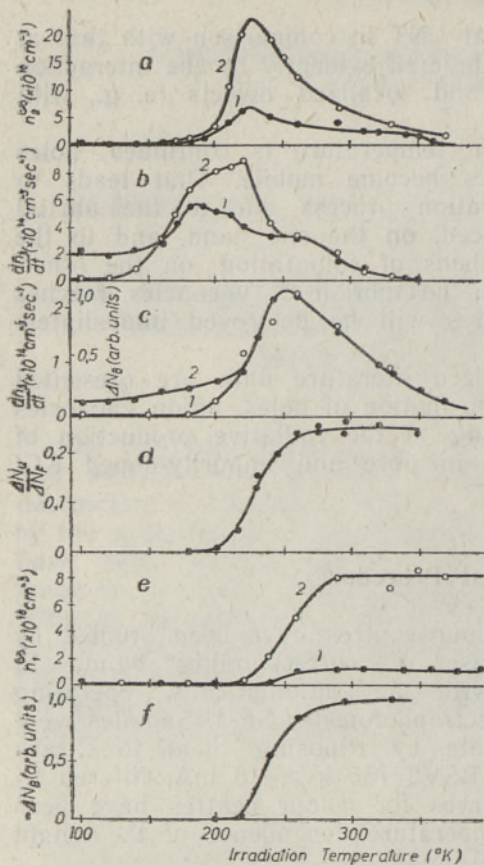


Fig. 1. Temperature dependences of the efficiency of various processes of colour centre production in KCl crystals:

a — the 2nd stage for F-centres (1 — pure, 2 — Pb-doped);
 b — the 3rd (linear) stage for F-centres (1 — pure, 2 — Ag-doped);
 c — B-centres in Ag-doped crystal. 1 — the number of centres produced by complete optical bleaching of F- and E-centres in sample preliminarily x-rayed for 90 min at RT, 2 — the 3rd stage of radiative production;
 d — the number of U-centres produced per optically bleached F-centre in H-doped sample preliminarily x-rayed for 30 min at RT;
 e — the 1st stage for F-centres (1 — pure, 2 — H-doped);
 f — the number of B-centres destroyed by x-rays during 15 min in KCl (Ca, Ag) crystal preliminarily x-rayed for 30 min at RT and optically bleached in F- and E-bands.

The main experimental results obtained are demonstrated in Fig. 1. Some of them are preliminarily presented and discussed in papers [8, 10, 11].

The 1st stage of F-centre production is due to the radiative conversion of U- (and OH⁻)-centres into F-centres [8, 11]. In Fig. 1, n_1 vs T is plotted.

At the 2nd stage, F-centres are produced as generally accepted (see e. g. [12]) on account of vacancies existing in crystals as clusters before irradiation. In Fig. 1, a , n_2 vs T is plotted.

The 3rd (linear) stage of colouration is due to new vacancies and F-centres produced by radiation, and it evidently arises as a result of the decay of excitons in regular position of the lattice [1, 2]. In Fig. 1, b dn_3/dt vs T is plotted.

Analogical stages have been stated in the B-centre (Ag⁻ ions at anion positions [13]) growth curves in KCl(Ag), the 3rd one being overwhelming in this case (see also [1, 10, 14]). In Fig. 1, c , dn_3/dt vs T for B-centres is plotted as well as ΔN_B , the number of B-centres produced by optical destroying of F- and E-centres in KCl(Ag) preliminarily x-rayed at RT.

The effect of the destruction of B-centres in KCl (Ca, Ag) by x-rays stated in papers [15] has been studied by us, too. An extra number of B-centres has been produced by an optical bleaching of F- and E-centres in samples preliminarily x-rayed for 90 min at RT. If such a sample is reirradiated with x-rays, the number of B-centres decreases. The number of B-centres, $-\Delta N_B$, destroyed during reirradiation of 15 min, versus reirradiation temperature is plotted in Fig. 1, f . Control experiments have shown that if the sample is kept at RT without reirradiation, N_B is not markedly altered during that time.

Finally, the reconstruction of U-centres by an optical bleaching of F-centres in KCl(H) has been studied. Samples have been x-rayed at RT for 30 min. During the following optical bleaching of F-centres, the U-centres are reconstructed. The number of U-centres, ΔN_U , per number of bleached F-centres, $-\Delta N_F$, versus temperature of the bleaching is plotted in Fig. 1, d .

4. Discussion

4.1. On the role of mobile holes in the irradiation-induced colouration

Beginning with the Känzig's pioneer experiments [16], it has been shown in a number of papers [17-22] that the physical phenomena in KCl crystals connected with the migration of thermalized holes proceed at temperatures of about 200°K and higher. In Fig 2, some of the experimental results confirming the above are plotted. One can see that in the temperature range of about 200°K, a considerable decrease of the V_K -centre paramagnetical [16,22] and optical [18] absorption occurs. At the same temperatures, the number of centres for the production of which the trapping of holes on impurity ions is necessary, sharply increases [22], and corresponding thermoluminescence appears [18-21]. The temperatures at which the efficiency of the processes described here increases with raising temperature most sharply lay in the interval of 195-215°K, depending, to some extent, on the nature of the process and on the concentration of trapping centres for holes. The mean temperature of this interval, 205°K, may be called the hole delocalization temperature in KCl crystals. Physically it means the temperature at which the phenomena connected with the migration of thermalized holes become observable.

In the same temperature range, the processes causing the 2nd stage of radiative colouration become effective (Fig. 2, e). The coincidence

Fig. 2. Temperature dependences of the efficiency of various processes connected with the migration of holes in KCl crystals:

a — paramagnetic absorption of V_K -centres during the heating of samples (1 — pure, 2 — Ag-doped, 3 — Tl-doped) x-rayed at LNT [22];

b — paramagnetic absorption of Ag^{++} -centres (1) and $ClBr^-$ -centres (2) during the heating of Ag-doped samples x-rayed at LNT [22];

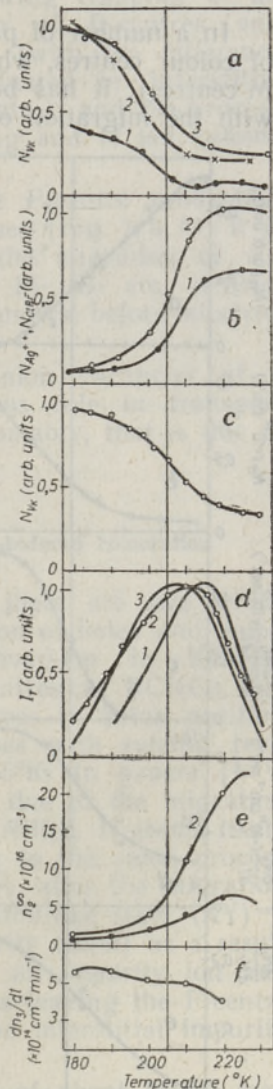
c — optical absorption of V_K -centres during the heating of Pb-doped sample x-rayed at LNT [18];

d — thermoluminescence during the heating of Ag-doped [20] (1), Pb-doped [18] (2) and Tl-doped [21] (3) samples x-rayed at LNT;

e — see Fig. 1, a;

f — see Fig. 1, b, 1.

The vertical line indicates the hole delocalization temperature.



of this kind allows to us to assert confidently that some of F-centre production processes include the migration of holes. We hold the point of view that the F-centre production at this colouration stage occurs as a result of migration of holes to vacancy clusters with a following separation of single vacancies from clusters by nonradiative recombinations of electrons and holes in their vicinity [23, 24].

In the same temperature region, the efficiency of F-centre production on the 3rd colouration stage decreases slightly (Fig. 2, f). Obviously, that is the result of the destruction of a part of F-centres by holes. In KCl(Ag) this process is hindered by the capture of holes at Ag^{+} - and Ag^0 -centres.

4.2. On the role of mobile vacancies in the irradiation-induced colouration

In a number of papers [25–27] devoted to the study of the production of colour centres, which include F-centres as components (Z_1 -, F_A - and M-centres), it has been shown that the physical processes connected with the migration of anion vacancies in KCl crystals proceed at temperatures of about 200–250°K and higher.

In Fig. 3 one can see that in this temperature region radiatively produced α -centres decay [27] and the production of M- and F_A -centres by the optical bleaching of F-centres becomes effective [25, 26]. All these processes contain a migration of anion vacancies.

The results obtained by us indicate that the sharp increase of the efficiency of B-centre production in KCl(Ag) by x-rays (see also [10, 11]) and by the optical bleaching of F- and E-centres in preliminarily x-rayed samples occurs in the same temperature range (Fig. 3, d). The same may be said about the efficiency of the reconstruction of U-centres by the optical bleaching of F-centres in x-rayed KCl(H) samples (Fig. 3, e).

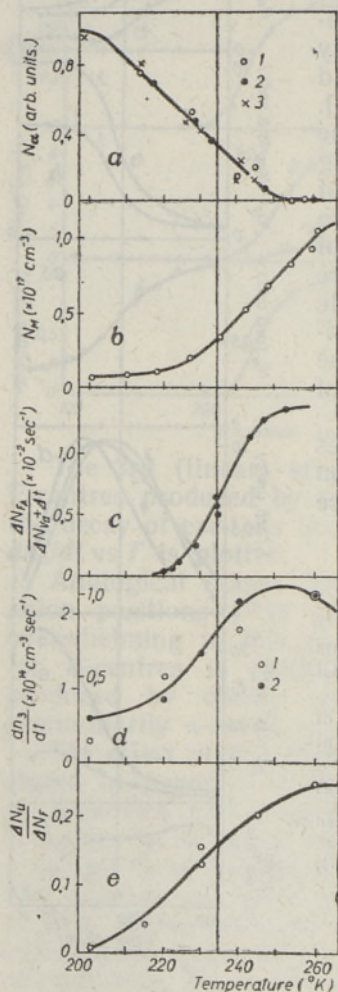


Fig. 3. Temperature dependences of the efficiency of various processes connected with the migration of anion vacancies in KCl crystals:

- a — thermal decay of α -centres produced by optical bleaching of F-centres in x-rayed samples (1 — pure, 2 — Li-doped, 3 — Sr-doped) [27];
- b — production of M-centres during the heating of samples x-rayed at LNT [25];
- c — production of F_A -centres by optical bleaching of F-centres in additionally coloured Na-doped sample [26];
- d — see Fig. 1, c;
- e — see Fig. 1, d.

The vertical line indicates the anion vacancy delocalization temperature.

The temperatures at which the efficiency of the processes described increases most sharply with raising temperature, lay in the interval of 225–245°K. Such a coincidence allows to conclude that all these processes are connected with the migration of anion vacancies and

mark the mean point of this interval, 235°K, as the anion vacancy delocalization temperature in KCl crystals. The physical meaning of this temperature is analogical to that of the hole delocalization temperature (see Sec. 4.1).

As to the detailed mechanism of the processes concerned, in the case of production of M^- , F_A^- and Z_1 -centres ($(v_a^+e^-)_2$, $M_c^+v_a^+e^-$ and $M_c^{++}v_c^-v_a^+e^-$, respectively, M_c being the impurity metal ion in the cation position of the lattice) it consists evidently in the migration of v_a^+ to the other partner together with the following trapping of an electron [27]. In the cases of the production of B-centres and reconstruction of U-centres, an analogical centre (with the difference that Ag and H ions or atoms are probably situated in interstitial positions) acts as the intermediate state (latent centre), and the process is completed by the transition of the interstitial Ag and H ion (atom) into the anion vacancy.

In the temperature region examined here, the F-centre production yield at the 2nd and 3rd colouration stages decreases (Fig. 1, a, b). It is also natural to connect these phenomena with the migration of v_a^+ (competition from the side of the production of M^- , B- etc. centres, joining of produced and released vacancies to clusters before electron capture).

At first sight it seems unintelligible that anion vacancies of a comparatively high mobility play an unpretentious role in transport phenomena in alkali halides (see e. g. [28]). Presumably, that is due to the high probability of joining them to clusters.

4.3. On the role of mobile excitons in the irradiation-induced colouration

Among the processes studied in this paper, there are two which are hard to explain, like the results of the migration of holes and anion vacancies. These are the radiative $U \rightarrow F$ conversion in KCl(H) (Fig. 1, e) and the radiative destruction of B-centres in KCl(Ca, Ag) (Fig. 1, f). In both cases, the destruction of centres in anion position occurs. The efficiency of those processes increases with raising temperature most sharply in the interval of 240—255°K. In papers [8, 11] the guess that the radiative $U \rightarrow F$ conversion is due to the migration of excitons to U-centres has been expressed and justified. It seems likely that the radiative destruction of B-centres is due to the same process [15]. It is reasonable to suppose that in both cases, after the migration of an exciton to the corresponding centre, an exciton-like state $(XY)^=*$ arises (X being a regular anion and Y — an impurity anion) as a result of sp-hybridization of an s-like outer electron of an impurity ion and a p-like one of a regular ion. This state dissociates leaving the F-centre ($v_a^+e^-$) in the position of the destroyed centre and interstitial impurity atom (Y_i^0).

If this assumption is correct, the temperature of about 250°K may be called the exciton delocalization temperature in KCl crystals. At this temperature excitons become mobile enough to interact with lattice defects before decay.

If one assumes excitons to have the same mobility as holes, then they can migrate with the velocity of about 400 jumps/sec at a temperature of 250°K [29]. It is too low to interact with impurities of about 10^{16} — 10^{17} ions/cm³ concentration, taking account of the exciton's

lifetime (about 10^{-6} sec). It seems likely that the lattice around the moving excitons is relaxed to a smaller extent than that around holes, causing the greater mobility of the former.

Acknowledgements

The authors would like to thank Prof. Ch. Lushchik for most valuable discussion and M. Muradova for carrying out some of the measurements.

REFERENCES

1. Лушчик Ч. Б., Вале Г. К., Эланго М. А., Изв. АН ЭССР, Сер. физ., **31**, 820 (1967).
2. Лушчик Ч. Б., Витол И. К., Эланго М. А., ФТТ, **10**, 2753 (1968).
3. Royce V. S. H., Progr. Solid State Chem., **4**, 213 (1967).
4. Rabin H., Klick C. C., Phys. Rev., **117**, 1005 (1960).
5. Behr A., Peisl H., Waidelich W., Phys. Letters, **24A**, 379 (1967).
6. Витол И. К., Боган Я. Р., Зирап В. Е., Изв. АН СССР, Сер. физ., **31**, 854 (1967).
7. Эланго М. А., Тр. Ин-та физ. и астрон. АН ЭССР, № 12, 197 (1960).
8. Мурадов С. М., Мурадова М. Х., Яансон Н. А., Эланго М. А., ФТТ, **11**, 1582 (1969).
9. Alvarez Rivas J. L., Levy P. W., Phys. Rev., **162**, 816 (1967).
10. Мурадов С. М., Эланго М. А., ФТТ, **10**, 3218 (1968).
11. Muradov S., Elango M., Color Centers in Alkali Halides, 1968 Intern. Symp., Rome, 1968, p. 205.
12. Schulman J. H., Compton W. D., Color Centers in Solids, Pergamon Press, N. Y., 1962.
13. Kleemann W., Z. Phys., **214**, 285 (1968).
14. Вале Г. К., Тр. Ин-та физ. и астрон. АН ЭССР, № 28, 93 (1964).
15. Lushchik Ch. B., Zaitov F. N., Kark V. Ya., Teiss L. A., Jaek I. V., Proc. 5th Conf. Luminescence, Tartu, 1957, p. 75; Lushchik Ch. B., Liidja G. G., Proc. 7th Conf. Luminescence, Tartu, 1959, p. 101.
16. Känzig W., Phys. Rev., **99**, 1890 (1955).
17. Delbecq C. J., Smaller B., Yuster P. H., Phys. Rev., **111**, 1235 (1958).
18. Neubert T. J., Refiner J. A., J. Chem. Phys., **36**, 2780 (1962).
19. Золотарев Г. К., Лушчик Ч. Б., Соовик Т. А., Яэк И. В., Эланго М. А., Изв. АН СССР, Сер. физ., **29**, 36 (1965).
20. Золотарев Г. К., Тр. Ин-та физ. и астрон. АН ЭССР, № 23, 175 (1963).
21. Delbecq C. J., Ghush A. K., Yuster P. H., Phys. Rev., **150**, 599 (1966).
22. Пунг Л. А., Халдре Ю. Ю., Изв. АН СССР, Сер. физ., **30**, 1443, 1446 (1966).
23. Эланго М. А., Тр. Ин-та физ. и астрон. АН ЭССР, № 26, 182 (1964).
24. Лушчик Ч. Б., Лийдья Г. Г., Эланго М. А., ФТТ, **6**, 2256 (1964).
25. Rabin H., J. Phys. Soc. Japan, **18**, Suppl. III, 334 (1963).
26. Härtel H., Lüty F., Z. Phys., **177**, 369 (1964); **182**, 111 (1964).
27. Giultani G., J. Phys. Chem. Solids, **30**, 217 (1969).
28. Lidiard A., Ionic Conductivity, Springer-Verlag, Berlin, 1957.
29. Keller F. J., Murray R. B., Abraham M. M., Weeks R. A., Phys. Rev., **154**, 812 (1967).

Academy of Sciences of the Estonian SSR,
Institute of Physics and Astronomy

Received
21/VIII 1969

S. MURADOV, M. ELANGO

LIIKUVATE AUKUDE, ANIOONVAKANTSIDE JA EKSITONIDE OSAST KCl KRISTALLIDE RADIATSIOONILISES VÄRVIMISES

Uuriti F-tsentrite radiatsioonilist loomist KCl, KCl(Ag), KCl(Pb) ja KCl(H) kristallides, B-tsentrite radiatsioonilist loomist ja lagundamist KCl(Ag) kristallides ning U-tsentrite loomist F-tsentrite optilisel lagundamisel eelnevalt kiiritatud KCl(H) kristallides temperatuurivahemikus 80—400°K.

Selgitati välja protsessid, mis on seotud liikuvate aukude (F-tsentrite loomise teine staadium), anioonvakantside (B-tsentrite loomine, optiline F → U-muundamine) ja eksitonidega (F-tsentrite loomise esimene staadium, B-tsentrite radiatsiooniline lagundamine).

Määрати aukude anioonvakantside ja eksitonide delokaliseerumise temperatuurid KCl kristallides, mis olid vastavalt 205, 235 ja 250°K.

С. МУРАДОВ, М. ЭЛАНГО

О РОЛИ ПОДВИЖНЫХ ДЫРОК, АНИОННЫХ ВАКАНСИИ И ЭКСИТОНОВ В РАДИАЦИОННОМ ОКРАШИВАНИИ КРИСТАЛЛОВ KCl

Исследовалось радиационное создание F-центров в кристаллах KCl, KCl-Ag, KCl-Pb и KCl-H и B-центров в кристаллах KCl-Ag, а также радиационное разрушение B-центров в кристаллах KCl-Ca, Ag и создание U-центров при оптическом разрушении F-центров в предварительно облученных кристаллах KCl-H в интервале температур 80—400°K.

Кривые нарастания числа F-центров разделены на три стадии, две из которых насыщаются со временем облучения, а третья идет с постоянной во времени скоростью. Путем сравнения оригинальных и литературных данных показано, что вторая стадия создания F-центров связана с миграцией дырок, создание B-центров и оптическое F → U-превращение — с миграцией анионных вакансий, первая стадия создания F-центров и радиационное разрушение B-центров — с миграцией экситонов.

На основе температурных зависимостей указанных процессов определены температуры делокализации анионных вакансий (235°K) и экситонов (250°K) в кристаллах KCl.

С учетом вытекающих из данной работы реальных подвижностей дырок, анионных вакансий и экситонов удается понять все основные закономерности структурно-чувствительного окрашивания кристаллов KCl.