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Trap Distribution Changes in Quenched KCl by Heating or Pressure

By

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With 2 Figures in the Text

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Pure Potassium chloride, when quenched rapidly from melt shows pronounced glow peak at 250 °K. The intensity of the glow peak has been found to decrease by heating the specimen to around 450 °K, or by subjecting it to pressure. A qualitative interpretation of these effects has been offered on the basis of quenched — in cation — anion vacancy pairs.

Introduction

The present work is concerned with examining the effects of temperature as well as pressure, as an independent variable, in the thermoluminescence studies of quenched KCl. The thermoluminescence curve consists of a principal glow peak at 250 °K and few subsidiary peaks. More or less similar work was reported in a previous paper[1] but the significance of the results obtained was not clear. Speculations presented in it are modified in this paper to fit the results qualitatively. It is suggested that the electron traps at 250 °K are due to quenched-in cation-anion vacancy pairs. The content of thermally produced dislocations in the microcrystals of the quenched specimen is expected to be high. In this respect the measurements have considerable importance, since it is presumed that these dislocations act as annihilation centres for the vacancy pairs. The requisite pair migration energy is suggested to have been provided either by heating or to a certain extent by pressure.

Experimental

In the preparation of the sample, the melt of pure KCl in a platinum crucible was transferred directly into a silica dish containing liquid nitrogen. The specimen so obtained was a compact, shapeless, polycrystalline mass of KCl. The specimen used in the experiments were prepared on the day on which measurements were made.

The experimental technique used has been described in an earlier paper[2]. The phosphor was excited at liquid nitrogen temperature, with

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radiations from a spark between aluminium electrodes. Subsequently it was warmed, at the rate of 0.15 deg. sec^{-1}, to about 450 °K and then returned immediately to liquid nitrogen temperature for re-measurement of the glow curve. In this way the phosphor was subjected to four cyclical successions of heating and cooling. The resulting glow curves have been recorded with a RCA 931 A photomultiplier in conjunction with a d. c. amplifier and a mirror galvanometer.

For comparative study of the trap distribution in pressed and unpressed quenched KCl, the specimens were prepared from equal quantity of KCl by weight. Along with the other conditions of the experiment, the surface areas of the specimens exposed to irradiation were also kept nearly equal. The magnitude of pressure used for compressing was of the order of 1000 psi.

Results

Since the positions of the peaks exhibited by different curves in Figs. 1 and 2 somewhat vary, the temperature values 250°, 300°, 350°, and 400 °K are hereinafter referred to indicate the principal trap depths observed in the figures.

It is seen from Fig. 1 that quenched KCl exhibits a pronounced glow peak at 250 °K and two subsidiary peaks around 300 and 400 °K. With the exception of a small rise in the height of 400 °K peak at the end of second run, the heights of the glow peaks in general decrease at the end of each heating run. Fig. 2 shows that when quenched KCl is pressed, the trap distribution changes. The peak at 250 °K is suppressed and those at 300 and 350 °K become strongly marked.

Discussion

Results reported in the previous paper[1] indicate that the KCl melt, quenched either in air or in vacuum, exhibits same glow peaks. One may therefore infer that these peaks are not the effects of contamination by air. Further, experiments carried out with "Specpure" and "Reagent" grade KCl makes a categorical assignment of these effects to impurity centres improbable. It is suggested that the trapping centres involved at 250 °K are cation-anion vacancy pairs with the cation and anion vacancies residing on two adjacent sites in the lattice. So far, it has not been possible to obtain experimental evidence to support the existence of vacancy pairs in the alkali halides. However, vacancy pairs have their importance in the understanding of Colour Centre reactions[3] and anion diffusion[4,5] in

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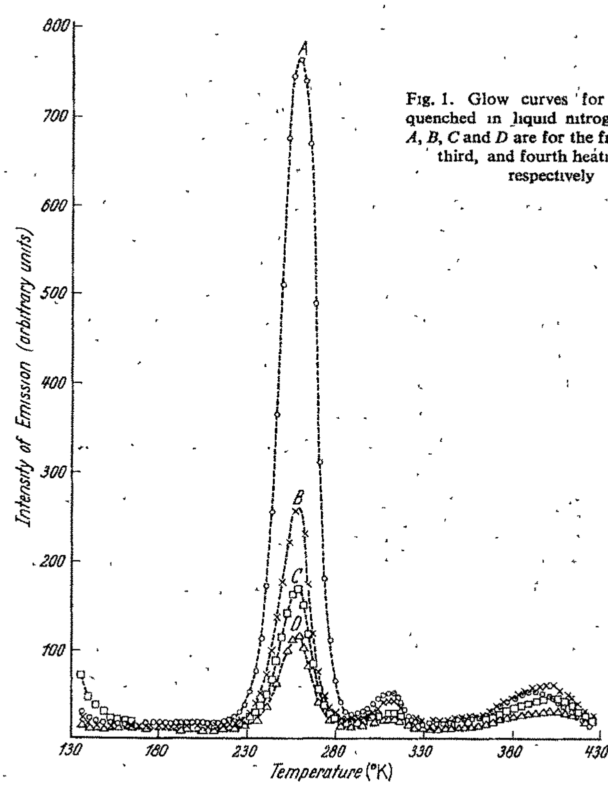

Fig. 1. Glow curves for KCl melt, quenched in liquid nitrogen. Curves *A*, *B*, *C* and *D* are for the first, second, third, and fourth heating runs respectively

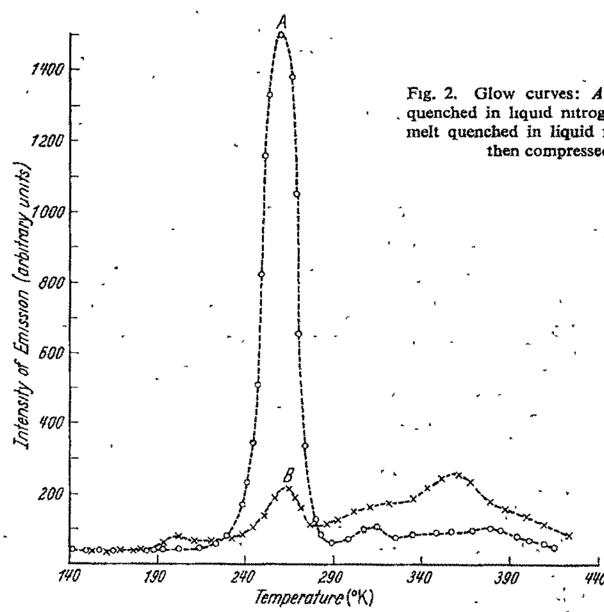

Fig. 2. Glow curves: *A*: KCl melt quenched in liquid nitrogen; *B*: KCl melt quenched in liquid nitrogen and then compressed

alkali halides. Defects present in the alkali halides, at a temperature as high as the melting point, can be only Schottky defects. It has been shown that the mobility of negative ion vacancies is much less compared to positive ion vacancies[6, 7]. If a positive ion vacancy approaches a few atom distances from a negative ion vacancy, they will exert a strong Coulomb attraction on each other and may join to form a neutral pair. Thus, during the quench, most of the vacancies may get associated into pairs and some in higher aggregates. One may then picture the quenched specimen to contain many neutral pairs in equilibrium with dissociated vacancies.

The decrease in 250 °K traps, by heating to about 450 °K, suggests that the trapping centres are not thermally stable at that temperature. Results reported by THARMALINGAM et al.[8] indicate that the mobilities of vacancy pairs in the room temperature region are not much higher than those of single anion vacancies in this region. Hence there cannot exist any possibility for the vacancy pairs to anneal out to the surface when the specimen is heated to about 450 °K. Since the distance a vacancy pair can move is thus limited by its diffusion coefficient, it is suggested that during the heating, a vacancy pair diffuses to a dislocation situated a few atom distances away and gets annihilated. Quenching a specimen from melting point to liquid nitrogen temperature imparts a considerable thermal-shock to the specimen. Hence the dislocations introduced in the microcrystals of the specimen by thermal stresses should be large in number and their possible effects should be equally significant. The thermal energy provided by heating may be sufficient to stimulate migration of a pair to a nearby dislocation. Since the dislocations act as sinks for vacancies, the vacancy pair gets destroyed at the dislocation site. The decrease in the concentration of vacancy pairs would naturally involve a corresponding decrease in the concentration of free vacancies in equilibrium with the pairs.

In Fig. 1 it is observed that the three glow peaks are unequally influenced by the successive runs of heating and cooling. This suggests that these traps do not have the same nature. It is proposed that the 300 °K trap is due to single negative ion vacancies and the 400 °K trap is due to higher aggregates of vancancies probably formed by trapping of vacancy pairs. The latter, which suggests inter-trap conversion, is supported by the increase in the 400 °K trap at the end of the second run. Since the increase in the 400 °K trap is not matched by the corresponding decrease in the 250 °K trap, it appears that only a small fraction of the vacancy pairs is involved in the conversion to higher

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aggregates. One may, in general, say that as a result of heating there is decrease in all the traps.

Fig. 2 shows that when the quenched specimen is compressed, the 250 °K traps decrease in number and those at 300 and 350 °K considerably enhanced. In this case the change in trap distribution obviously indicates that a significant number of vacancy pairs takes part in the conversion to deeper traps and a few disappear, probably by diffusion to dislocations. When the specimen is compressed the dislocations will naturally be set in motion. It is proposed that the heat generated by a passing dislocation may be sufficient to cause the removal of the electron from the Cl^- ion to the neighbouring halide ion vacancy of opposite charge. Trapping of an electron by the pair will break up the pair and the positive ion vacancy will be free to move. Presumably, the dissociated positive ion vacancy diffuses away and associates to form higher aggregates attributable to 350 °K trap. It may also contribute to form a hole-trap at lower temperatures. Since the number of negative ion vacancies, comparatively immobile, increases with the dissociation of positive ion vacancies, it is to be expected that the 300 °K trap should increase, as observed in Fig. 2. The identification of 300 °K trap with negative ion vacancies is also corroborated by the results reported recently[9].

Thus the decrease in the intensity of 250 °K glow peak in quenched KCl, by heating or by pressure, is understandable in a general sense on the basis of vacancy pair model for electron traps at that temperature.

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ELECTRON TRAPS IN KCl QUENCHED FROM THE MELT

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Since the heat treatment or plastic deformation alters the vacancy content in alkali halides, one might expect that their effects are tied up with the general problem of the production and annihilation or transformation into higher aggregates of vacancies. In view of this it has been proposed in an earlier paper [1)] that the phosphorescence in KCl:Tl, X-irradiated at room-temperature, is the result of the recombination of the electrons freed from negative ion vacancies and the holes at Tl centres. In a subsequent paper [2)] it has been argued that the pronounced glow peak at 250°K in KCl, quenched rapidly from melt, is due to quenched-in cation-anion vacancy pairs. On the basis of this model it has been possible to offer qualitative interpretation to the effects of heat and mechanical treatment on the trap distribution changes in the phosphor. In the light of the proposed vacancy pair concept we discuss here the occurrence of a pronounced glow peak at 250°K, reported by Braner and Halperin [3)], in X-irradiated KCl. They observed that the glow curve exhibited by virgin KCl crystal undergoes changes in the intensity distribution of the peaks if the crystal is subjected to subsequent cycles of X-irradiation (at liquid nitrogen temperature), heating (to about 500°K) and then cooling. It was observed that 40 cycles of heating and cooling and 5 hours of X-irradiation resulted in enormous increase in the intensity of 250°K glow peaks (fig. 4 in ref. 3). This result is consistent with the vacancy pair model as discussed below.

Though the present state of understanding of the nature of the defects formed by X-irradiation at liquid nitrogen temperature is not quite satisfactory, most of the speculations [4)] concerning colouration at this temperature assume the production of F-centres from Schottky defects. Because of the requirement of electrical neutrality of the crystal, cation and anion vacancies may therefore be continually generated by X-irradiation. After each dose of X-irradiation, Braner and Halperin heated the crystal to about 500°K for the record of the glow curve. The thermal energy provided by heating would be sufficient to stimulate the migration of vacancies. During migration, if a positive ion vacancy and a negative ion vacancy arrive at a distance of few lattice spaces from each other they will, as a result of strong Coulomb attraction, associate themselves to form a neutral pair. Thus, due to cyclical succession of X-irradiation, heating, and cooling the concentration of vacancy pairs in the crystal would increase, which, according to vacancy pair model, would enhance the 250°K glow peak.

Braner and Halperin suggest that the thermal activation energy for the glow peak at 250°K seems to fit the gap between the valence band and the *α-band. On this view it is difficult to offer an explanation for the observed decrease in the intensity of 250°K glow peak and the enhancement in the intensity of certain peaks at higher and lower temperatures after subjecting the quenched KCl specimen to pressure. On the other hand, the vacancy pair model is well supported by theoretical considerations [5,6)] which indicate that Schottky vacancies predominate in alkali halides and that near melting point, approximately 0.1% of the lattice sites are vacant. Further, at temperatures as high as the melting point, these vacancies should associate into cation-anion vacancy pairs relatively more quickly, thereby eliminating isolated vacancies. *alpha-

The present model can also explain the occurrence of the pronounced glow peak at 250°K observed by Johnson and Williams [7)] in their study of the electron traps in KCl:Tl. Since the phosphors used in the study were prepared by rapid fusion and cooling, one might expect a high concentration of vacancy pairs in the specimen. Excitation of the phosphor, at low temperature, probably transfers the electron from a chloride ion to the adjacent negative ion vacancy of the pair. During warm-up, at about 250°K the electron released from the trap recombines with the hole at the hole centre with the emission of a photon. Since the efficiency of such a luminescance is less, the excess recombination energy may be transferred to the closely situated substitutional Tl^+ ion. This would give rise to an emission characteristic of the Tl^+ centre and hence a pronounced glow peak at 250^oK.

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