Electron emission in the recombination of Frenkel defects

V. V. Bichevin and H. F. Käämbre

Institute of Physics, Academy of Sciences of the Estonian SSR

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A thermally stimulated electron emission from ionic crystals (KCl and NaCl:Ag), which accompanies a recombination of Frenkel defects at liquid-helium temperatures, has been observed.

A thermally stimulated electron emission is known to accompany the recombination of thermally delocalized hole V_k centers with electron centers $(Tl^0, F, F', \text{etc.})$. This electron emission is initiated by an ionization of electron centers which acquire energy released in recombination events. Our objective was to determine whether a recombination-associated thermally stimulated electron emission of this sort also occurs as Frenkel defects are annealed out. If it does, it would be of interest as a new source of information on these processes and as a manifestation of electron emission at extremely low temperatures.

The present experiments are carried out with single-crystal plates of KCl and NaCl:Ag, soldered with an indium alloy to the crystal holder of an ultrahigh-vacuum cryostat for emission studies.² The crystals, cooled to ≈ 5 K, are irradiated with x rays (W anode, 60 kV, Be windows, dose of 1–2 kGy). During the subsequent natural heating (≈ 7 K/min), the thermally stimulated electron emission and the thermally stimulated luminescence are measured simultaneously. The electron emission is detected with a VÉU-OT-8M secondary electron multiplier in electron-counting operation; the luminescence is measured with an FÉU-71 photomultiplier; and the temperature is measured with a KT372 transistor (within +1-2 K).

Figure 1 shows some typical temperature spectra of the electron emission and the luminescence. We know of no other observations of a thermally stimulated electron emission from dielectrics at such low temperatures (metals were studied in Ref. 3). There is a clear agreement between the peaks in the electron emission and in the luminescence 1 and also between the peaks in the luminescence in these experiments and those reported by other investigators who have studied the thermally stimulated luminescence along with thermal annealing of the I, α , F, H, and V_k centers in KCl and NaCl (Refs. 4–10 for example). We can therefore draw on those other results and conclusions in identifying the processes involved in the thermally stimulated electron emission. Since only the interstitial components of Frenkel defects acquire a mobility during heating from 5 K to 50 K—first the I centers and then the H centers—and a direct thermal ionization of electron centers is not possible, we believe that the thermally stimulated electron emission is initiated by mobile interstitials. The following defect-chemical reactions might occur and give rise to the thermally stimulated electron emission (see also Ref. 11):

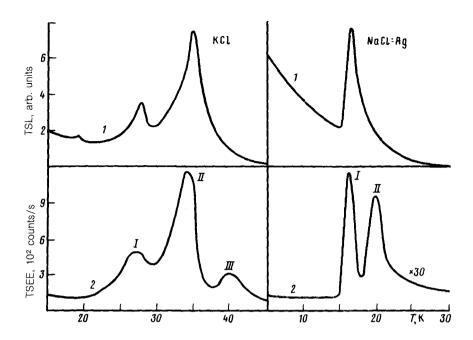


FIG. 1. Temperature spectra of (1) the thermal stimulated luminescence and (2) the thermally stimulated electron emission of KCl and NaCl:Ag (0.5 mole % in the melt). X—irradiated during cooling by liquid helium.

$$I + F \to R + e^- \tag{1.1}$$

$$H + F' \to R + e^- \tag{1.2}$$

$$I + \alpha \to R + \epsilon, \ \epsilon + E \to E^{\bullet} + e^{-} \tag{2.1}$$

$$H + F \mapsto R + \epsilon, \epsilon + E \to E^{\bullet} + e^{-}. \tag{2.2}$$

Here I and H are mobile interstitials; F, F', and α are F, F', and α centers; R is the regular lattice; e^- is a conduction electron; E is an electron center; E^{\bullet} is an ionized E; and ϵ is the energy released. Since the electrons e^- which appear in reactions (1.1)–(2.2) have an elevated energy, the hottest of them may be emitted. This emission might be facilitated by an electric field caused near the surface in the crystal by the x-ray photoemission during the irradiation. If the defects are annealed out at equal rates, the single-step reactions (1.1-2) are more effective for the thermally stimulated electron emission than the two-step reactions (2.1-2); processes (1.1-2) are more likely in the stages of the annealing out of separated, uncorrelated Frenkel pairs. The peak in the thermally stimulated electron emission probably stem from the following reactions. For KCl, I—(1.1)',(2.1); II—(1.1); II—(1.2),(1.1)'',(2.2). For NaCl:Ag, I—(1.1); II—(1.2),(1.1)'. Several of the reactions are shown in order of decreasing suggested probability; the primes on (1.1) indicate a different initial relative arrangement of the I and F centers. This interpretation is to be refined in future research, since it is slightly difficult to use data from the literature because of differences in experi-

mental conditions and discrepancies in the conclusions reached by different investigators.

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¹⁾Some peaks in the thermally stimulated luminescence which are not resolved in the present experiments, at \approx 40 K in KCl and at \approx 20 K in NaCl, are clearly seen in Refs. 4-6.

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