

# THE EFFECT OF POLARIZATION BY ELECTRIC FIELD ON THE SURFACE THERMOLUMINESCENCE OF LITHIUM FLUORIDE

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The work deals with the effect of polarization by electric field on the surface thermoluminescence yield of LiF in the presence of O<sub>2</sub>. It was noticed that the increase in the quantity of emitted light depends on the number of surface defects of the anion vacancy type.

## 1. Introduction

While investigating the influence of various physical factors on the adsorptivity of semiconductors it was noticed that when a semiconductive plate is placed in an external electric field the adsorptivity of one surface increases, whereas that of the other side decreases.

Volkenstein and collaborators [1] studied the luminescence induced by the processes of free atom and gas radical recombination at the surface of luminophors. During this work they found that placing the luminophor in a constant transverse electric field gives rise to a change in the intensity of the light from the same surface when the direction of the electric field is changed. For one field direction the number of free valences grew, whereas for the opposite it dropped, what involves a change in the quantity of adsorbed gas. These phenomena were observed in connection with semiconductive materials having a certain number of free current carriers at room temperature which in the case of gas adsorption also play the role of free valences.

Lithium fluoride, being a typical representative of ionic compounds with a very wide energy gap, does not have free current carriers at room temperature, but it features the thermoluminescence effect in the presence of oxygen, just like CaF<sub>2</sub> [2]. The lack of free current carriers, together with the appearance of thermoluminescence and not photoluminescence, made it necessary to apply a different method of examining the effect of an electric field on adsorption properties than that applied in an earlier work [1].

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## 2. Temperature dependence of conductivity

As mentioned in the Introduction, the number of electrons in the conduction band of an insulator is so small that it may be well neglected. Therefore, it should be assumed that in such case electric current is conducted by positively or negatively charged ions. In a crystal where all ions occupy their proper positions ion motion is impossible because no ion could be displaced without leaving its correct structural position. It may be concluded, hence, that then interstitial ions or ionic vacancies are charge carriers.

Ionic conduction caused by the motion of univalent ions of one sign is expressed by the relation

$$\sigma_j = \sigma_0 e^{-\frac{E_0}{kT}} \quad (1)$$

where  $E_0$  is the energy of defect creation and its subsequent migration.

Formula (1) can be presented in graphic form by taking the logarithms of both sides,

$$\lg \sigma = \lg \sigma_0 - 0.43 \frac{E_0}{kT} \quad (2)$$

Laying  $1000/T$  on the abscissa axis and  $\lg \sigma$  on the ordinate axis we get a straight line of slope which determines the energy  $E_0$  in electron-volts,

$$E_0 = 0.2 \operatorname{tg} \varphi \quad (3)$$

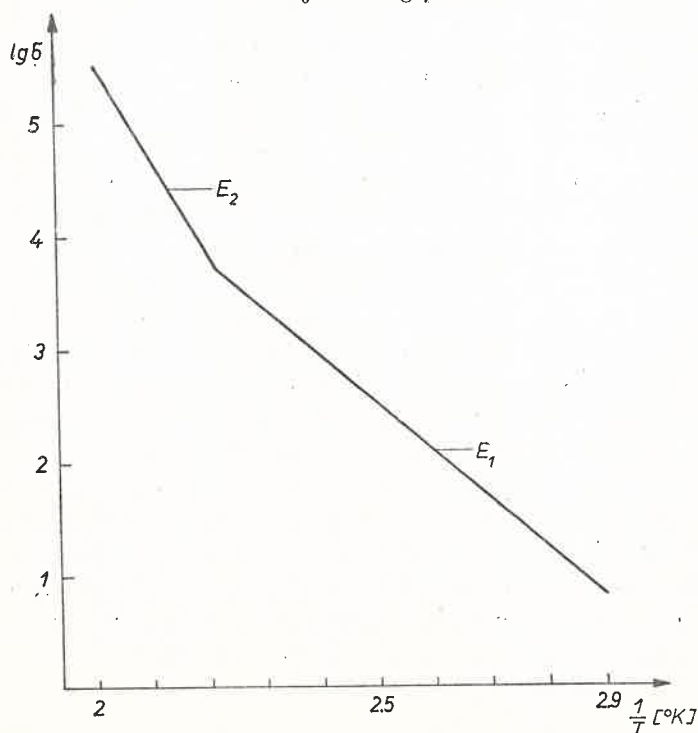


Fig. 1. Temperature dependence of electric conductivity of lithium fluoride crystal

Figure 1 presents the curve of  $\lg \sigma$  as a function of reciprocal temperature for a single crystal of lithium fluoride. As is seen in the figure, the graph consists of two rectilinear segments. Each one of these corresponds to a different energy  $E_0$ . For lithium fluoride these values are  $E_1 = 0.85$  eV in the low temperature range and  $E_2 = 1.62$  eV in the high temperature range. According to Refs [3, 4], the different slopes of the curves can be explained as follows. At low temperatures the thermal energy suffices to displace ions to existing vacancies, primarily associated with bivalent atom admixtures substituted in the crystalline structure in the place of univalent atoms. For every bivalent atom in the crystal there is one positive vacancy near it; this ensures charge compensation. At high temperatures the energy  $E_0$  is the sum of energy necessary for the formation of vacancies and displacement of ions to the positions of these vacancies.

Two electrodes were sputtered onto the opposite sides of a plane-parallel plate and an electric field was applied to them, as shown in Fig. 2. While the temperature of the plate was raised the current flowing through it was measured. After several measurements it was

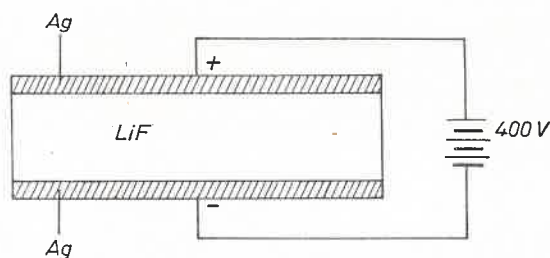


Fig. 2. Position of lithium fluoride crystal between the electrodes

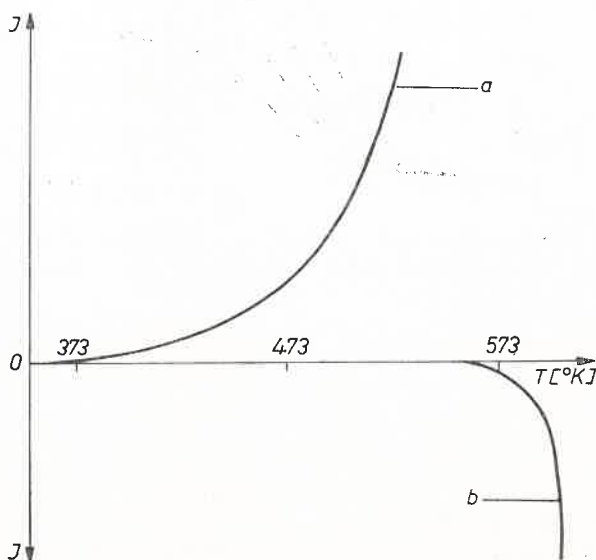


Fig. 3. High-voltage polarization. a) current at 400 V voltage, b) shorting current

noticed that the positive electrode becomes completely blackened. An analysis revealed that silver fluoride became formed on the anode. Moreover, shining points of dimensions of the order of tenths of a millimeter appeared inside the crystal, while the crystal itself became darkened. When such a crystal, after it cooled down, was annealed again with the circuit shorted, a flow of oppositely directed current was observed. The intensity of this current was low and shows up at a higher temperature (Fig. 3). Subsequent annealings decreased current intensity, and after four thermal operations the current dropped to nil.

### 3. Thermoluminescence of lithium fluoride

The quantity of light emitted in the thermoluminescence process by a single crystal plate of lithium fluoride is affected by the following parameters: oxygen pressure in ambient atmosphere, its value when it acts mechanically, and the temperature and time of storage of the lithium fluoride between two annealings if it is not submitted to mechanical action. Hence, leaving a lithium fluoride plate under conditions of  $T = \text{constant}$ ,  $P_{O_2} = \text{constant}$  and  $t = \text{constant}$  we will get the same quantity of light emitted during the thermoluminescence process for the successive annealings. If the crystal plate placed between the electrodes is submitted to the action of an electric field in the temperature range from 440 to 510°K and then proceed in the same way as for a plate not subjected to a field, we find that the

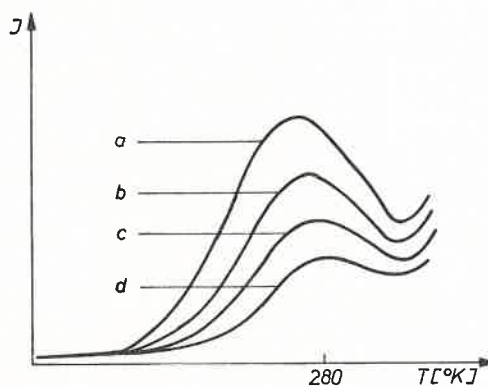


Fig. 4. Glow curves for LiF single crystal. *a*) first annealing after action of electric field, *b—c*) second and third annealing after action of electric field, *d*) before action of electric field

quantity of light emitted in the thermoluminescence process becomes changed. The magnitude of the change for the lower temperature range was several times smaller (three to five times, depending on the specimen of single crystal plate) than the change in quantity of light at the upper temperature range, the duration of electric field action remaining the same. At temperatures above 510°K there was breakdown in the crystal after applying voltage to the deposited electrodes. Analyzing the glow curves in Fig. 4 we see that the quantity of light emitted in the first annealing is much larger after the field acts than before it. Each successive annealing, under the same conditions of storage of the crystal, decreases the

quantity of emitted light. The glow curves presented in Fig. 4 correspond to the thermoluminescence of the entire crystal surface, without differentiating the surfaces in contact with the electrodes. Figure 5 presents the glow curves for the surfaces in contact with the positive and the negative electrodes. A greater quantity of light is emitted during the thermoluminescence process from the surface adjacent to the positive electrode than from the

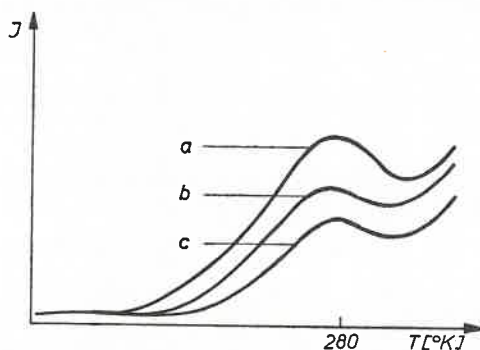


Fig. 5. Glow curves of LiF single crystal *a*) for surface on the side of the positive pole, *b*) for surface on the side of the negative pole, *c*) before action of electric field

surface adjacent to the negative electrode. Also, both of these surfaces emitted more light after electric field action than before it.

As the observed thermoluminescence is associated directly with adsorbed oxygen, it may be stated that the number of adsorbed particles is increased, and this is only possible when the number of adsorption centers becomes larger.

#### 4. Discussion of results

Freezing of ion concentration by rapid cooling, the appearance of a polarization EMF [3, 4, 5], and the chemical reaction on the anode give grounds for the implication that the number of defects on the surfaces adjacent to both the positive and negative electrodes becomes increased as compared with the initial state. On the surface from the side of the negative electrode there is an increase in the number of anion vacancies because of the diffusion of positive ions towards the cathode and negative ions towards the anode. The number of anion vacancies on the surface from the positive electrode side is increased as the outcome of the chemical reaction occurring on the electrode.

The relation between the quantity of light emitted in the thermoluminescence process and the change of ion concentration in the surface layer indicate that surface defects, and specifically anion vacancies, are the centers of oxygen adsorption. Should adsorption take place on a positive or negative ion, the quantity of thermoluminescent light should then increase for one surface and decrease for the other as compared with the initial quantity. However, as adsorption takes place on anion defects, the quantity of light emitted increases for both surfaces.

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