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THERMAL ACTIVATION ENERGY AND THE PROBLEM OF THE EMISSION MECHANISM DURING EXOELECTRON EMISSION FROM NaCl

PART III

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THERMAL ACTIVATION ENERGY AND THE PROBLEM OF THE EMISSION MECHANISM DURING EXOELECTRON EMISSION FROM NaCl

PART III

R. Seidl*

ABSTRACT. The activation energy of thermal destruction of F-centers in NaCl was measured by means of optical absorption. The resulting value of 2.1 eV is in good agreement with our results obtained by means of exoelectron emission and luminescence. The different possibilities of interpreting the origin of this energy are discussed. It was pointed out that there are now more arguments for its interpretation as the thermal dissociation energy of F-centers than for any other interpretation. This interpretation leads to good agreement with the theoretical results of Pekar. The limited validity of the Rose relation is pointed out.

1. Introduction

In the preceding parts of this work [1, 2], we studied the basis of the thermal activation energy in thermostimulated exoelectron emission from F-centers in NaCl. We have shown that, on the basis of the agreement of results from exoelectron, luminescence, and conductivity measurements [1, 2, 3, 4], on one hand, and the results of theory [5, 6], on the other hand, it can be explained as thermal ionization energy of the F-centers. But this statement is not sufficiently valid, because there are still some objections which must be handled. These are essentially the following facts: /73**

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1) The mechanism of exoelectron emission is not yet completely explained, so that under these conditions any statement based on the results of measuring exoelectron emission is to some extent questionable.

2) In luminescence, along with dissociation of color centers, there are also the varying concentrations in the activator level and the temperature-dependent probability of nonluminescent transitions which play a part.

Although it is difficult to expect that these possible complications might significantly affect our previous observations, it is reasonable to seek further confirmation. This is the principal purpose of the present work.

The weakest point of our previous determinations is in the questionable proportionality of the exoelectron emission and luminescence signals to the color center concentration during the whole decolorization process. Thus, it /74 seemed obvious to use the most direct possible method, optical absorption, for further investigations.

2. Experiments and Their Results

In the experiments, we investigated the thermal decolorization of NaCl monocrystals colored with x-rays by means of optical absorption at 4650 Å with a linear increase in temperature. All the measurements were performed in air. The light source was an incandescent tungsten filament lamp combined with a Zeiss reflection monochromator. The bandwidth used was some 10 Å. The stimulating x-radiation (35 kV, 15 mA) and the measuring light fell normally on the crystal surface. The light passing through the crystal was measured with a FEU 18A photomultiplier. The signals from the photomultiplier, as well as those from the thermocouple measuring the temperature of the crystal, were recorded on an EKB.

For the final processing, we needed a quantity proportional to the concentration of F-centers. The absorption coefficient itself is unfortunately

not suitable for this, because of its temperature dependence. The normalization of the absorption coefficient to a given reference temperature which is necessary can be determined either analytically or experimentally. We have chosen the second way, because it does not require the introduction of uncertain hypotheses. For this purpose, we have carried out a series of temperature jumps from various temperatures to the reference temperature with the colored crystal. The ratios for the limiting value of the absorption coefficient at each temperature are the desired correction factors which transform the absorption coefficients measured at various temperatures to the quantity μ proportional to the concentration of F-centers.

The thermal activation energy for the dissociation of the F-centers was established, just as for the luminescence measurements [2], by means of the equation

$$-\frac{dn}{dt} = np, \quad p = p_0 \exp^{-\varepsilon/kT} \tag{1}$$

Here n is the F-center concentration, p_0 the frequency factor, and α the thermal activation energy. By transformation of (1), we obtain

$$p_0 \exp^{-\varepsilon/kT} = \frac{\left(-\frac{dn}{dt}\right)}{n} b \tag{2}$$

where b is the rate of warming. This equation is suitable for Richardson's analysis* in the logarithmic form /75

$$\ln \frac{\left(-\frac{dn}{dt}\right)}{n} = \ln \frac{p_0}{b} - \frac{\varepsilon}{kT} \tag{3}$$

*Translator's Note: This pertains to the rotation of a body of magnetic material when a magnetic field is applied parallel to its axis.

In (3), μ was inserted directly in place of n. This is possible on the basis of the relation

$$\mu \sim n \tag{4}$$

We wish to mention that Equation (1) describes the strictly monomolecular decolorization process. The monomolecularity of the thermal decolorization process for the F-centers in NaCl has already been confirmed several times. Here, too, we will show further that our experimental results correspond well to Equation (1).

As the sample material, we used "pure" single crystals pulled from a melt.

Again, as in the measurements by means of exoelectron emission and luminescence, the major problem lay in the necessity of a simple decolorization process. In agreement with our earlier results, this was achieved by x-ray irradiation at the highest possible temperature. The decolorization curves after irradiation at different temperatures are shown in Figure 1. As is apparent, there is a complex decolorization process after coloring at lower temperatures. This depends strongly on the history of the sample. In this relation, it can be shown by absorption spectroscopy that we are in all phases of decolorization dealing with destruction of the F-centers. In this work, /76
we investigated the maximum temperature decolorization of the F-centers.

Figure 2 shows an example of the maximum temperature decolorization curve and the Richardson analysis for ε.

Table 1 gives examples of the values and mean value of ε determined from some experiments after irradiation at the temperature T_B.

It must expressly be emphasized that, in every case in which we established a significantly lower value of ε, the cause was the complexity of the decolorization process. This appeared from a large series of our measurements.

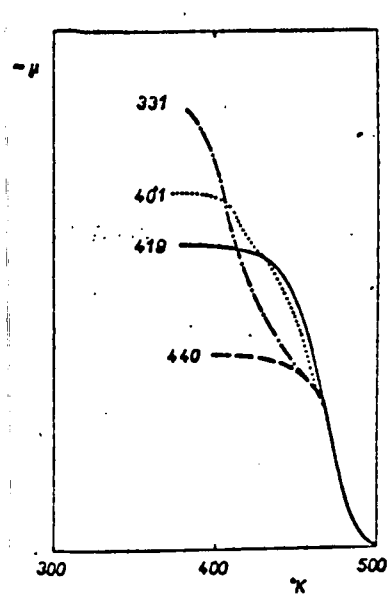

Figure 1. Course of the thermal decolorization of the F-centers, expressed by means of the normalized absorption coefficient μ. The irradiation temperatures T_B are given as parameters.

TABLE 1

Experiment No.	T_B [°K]	ε [eV]
403	470	2,07
404	470	2,13
408	467	2,03
409	469	2,07
418	472	1,92
531	461	1,94
728	447	2,03
Average value	—	2,07 ± 0,05

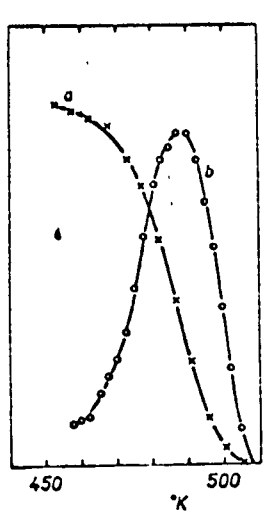

Figure 2a. Results of a measurement of high temperature decolorization. T_B = 469° K; $a \sim \mu$, $b \sim |d\mu/dT|$

The measurement was made with a linear temperature increase.

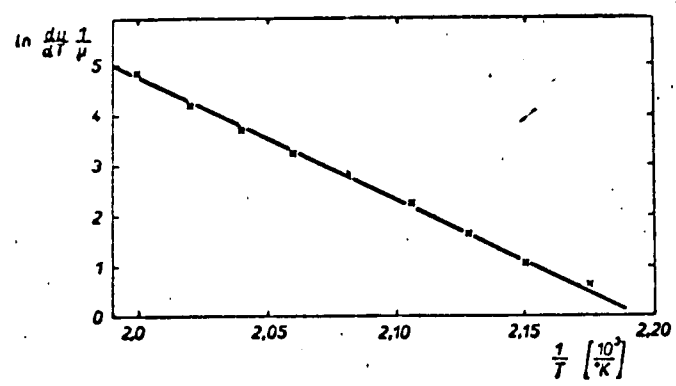

Figure 2b. The results from Figure 2a treated according to Equation (3).

ε = 2.07 eV

3. Discussion

The value determined above for the activation energy of thermal destruction of the F-centers shows that the objections to the results of exoelectron and luminescence measurements which were mentioned in the introduction have proved unimportant. All the values of ε obtained by these different phenomena are equal, within the limits of accuracy expected from the methodology. Here the value ε = 2.1 eV, and the value of the frequency factor, $p_0 = 10^{18}$ sec^{-1} [see (1)] obtained from ε and the temperature of the luminescence and exoelectron emission maxima, or from the temperature of the inflection point in the /77 curves of n(T), are verified from all points of view. This enables us to discuss the entire situation.

First let us turn to the problem of contradictions in the experimental values of different authors. The main group of authors whose results are in distinct contradiction to ours are Luscik [7], Zaitov, Lukancever, and Sidljarenko [8]. Almost without exception they have found analogous processes spread across a wider temperature range. That, obviously, leads to a significantly smaller value of ε ($\cong$1 eV) and, as a result, a smaller value of p_0. Now the question arises of the origin of this fact. There are at least three possibilities for finding a trivial explanation of this discrepancy. The first is that of gross inaccuracy of the temperature measurement. The second is inhomogeneity of the temperature in the sample, and the third is the development of a complex process on the basis of relations applying to a simple one. In comparison of the works, we find two of these [8, 9]. Here it is significant that Sidljarenko is listed as co-author of both works. From this, we can conclude that the same laboratory conditions, and in particular, similar sample material, prevailed. The results from [9] show clearly that they were dealing with a complex decolorization process in NaCl:Ag, but that it was analyzed as a simpler one in [8]. From comparison of the temperature ranges within which decolorization occurs according to [8] and [9], such great differences appear that they can hardly be explained as anything but the result of gross inaccuracy in temperature measurements. Under these circumstances, we cannot accept

the results of these authors as quantitatively correct. Seen from this viewpoint, the results of Luscik [7] are also questionable, as we already emphasized in [1]. As far as we know, there is no work by other authors with the glow curve method used quantitatively on NaCl in which sufficient attention was given to the homogeneity of the sample temperature and the simplicity of the decolorization process. Under these circumstances, we must ascribe greater weight to our multiply verified experimental results. /78

A more complex situation appears in interpretation of the values of ε and p_0. There are two opposing basic concepts here. On the basis of the first, we can explain ε as the true ionization energy of the F-centers, corresponding to the original concept of Randall and Wilkins [10]. With the second, which was originated by Zaitov et al. (e.g., [11]), ε is in contrast a complex quantity which results as a result of decolorization by chemical reactions among lattice defects.

Let us now consider the individual concepts separately.

As we have already shown in [2], the first interpretation of ε leads to good agreement with the theoretical values of Pekar [5] and Moskalenko [6]. This agreement was further supported by the experimental results mentioned above. But in spite of this, there is a great difficulty in the enormous value of p_0 ($\cong 10^{18}$ sec^{-1}). According to the relation of Rose [12] which was accepted by many other authors [13, 14],

$$\frac{p_0}{\Phi} \cong 10^{26}\left(\frac{T}{300}\right)^2 \tag{5}$$

(in this case, Φ is the effective cross section of the anion vacancy for capture of electrons) the extremely large frequency factor is the result of the overly large effective cross section of the anion vacancy, which must be about 10^{-8} cm^2 in our case. This would require a radius for the effective attractive force of the anion vacancy of about 10^{-4} cm. But this would have

the result that, even at a concentration of anion vacancies of about 10^{12} cm^{-3}, there would have to be overlapping of their spheres of action, and Equation (5) would lose its validity as a result of nonfulfillment of the initial hypotheses.

First, let us test the validity of the Rose relation. It was derived on the basis of comparing kinetic and statistical results. In doing so, Rose neglected not only the scattering of electrons in the conductivity band, but also the possibility that the conductivity electrons could occur in the polaron state. But this is the case, as Pekar [5] has shown, especially for the alkali halides. Thus, the Rose relation is nothing more than the result of the hypothesis of equality of a priori probabilities of the quantum states which is used in statistics. The correctness of this hypothesis, however, has not yet been demonstrated for the general case, and its validity is debatable, particularly in the case of electron transitions between the centers and the conduction band. The Rose relation thus does not provide a very valid interpretation of the cause of the gigantic frequency factor.

Nevertheless, some relation similar to Rose's must exist, linking the /79
frequency factor with the effective cross section of the color center. Let us stipulate the quite elementary postulate that there are in the crystal $M \exp(-\varepsilon/kT)$ energy fluctuations (where M is the number of lattice points, ε is the energy necessary to liberate electrons) which move through the crystal in the rhythm of the normal frequency factor ($\cong 10^{13}$ sec^{-1}). Then for the effective frequency factor we have

$$p_0 \cong 10^{13} \frac{\Phi_{ex}}{a_0^2} w_g \tag{6}$$

where Φ_{ex} is the effective cross section for stimulation, a_0 is the lattice constant, and w_g the geometric probability of electron transition. If we insert the mean value 10^{-15} cm^2 for a_0^2, we get

$$\frac{p_0}{\Phi_{ex}} \cong 10^{28} \tag{7}$$

It must be emphasized that Φ_{ex} is not identical with Φ because it is most probable that $\Phi > \Phi_{ex}$. The approximation Formula (7) provides us with further orientation in relation to the possibility of explaining ε as the thermal ionization energy of the F-centers. If we are dealing with a direct stimulation, then obviously the linear dimension of the F-center must be 10^{-5} cm. This is too great a value, because it would be nearly 10^3 times larger than the lattice constant. The situation is more favorable for ionization proceeding via an excited state. If we neglect the concentration of electrons in the excited state in comparison to those in the ground state, which is allowable in our case, then, if all transitions are thermally excited, we have the following relation for the over-all process and so for p from (1):

$$p = p_{12} \frac{p_{2\sigma}}{p_{21} + p_{2\sigma}} \tag{8}$$

where the excitation functions p_{ik} have the form $p_{ik} = p_{ik0} \exp(-\varepsilon_{ik}/kT)$ and the indices following individual states designate: 1 - the ground state; 2 - the excited state of the center; and σ - one of the conduction band or polaron states. Now if we express p_{ik0} on the basis of (6) and assume that $p_{21} \gg p_{2\sigma}$, which can be expected as a result of the progressivity of the Boltzmann exponential (see Figure 3), then we have

$$p_0 = \nu \frac{\Phi_{ex1}}{a_0^2} w_{g12} \frac{w_{g2\sigma}}{w_{g21}} \tag{9}$$

where ν is the true frequency factor ($\cong 10^{13}$ sec^{-1}). The quantities w_{g12} and w_{g21} are not identical. In the general case, also, the values of w_{gik} must not be proportional to the "phase surface". Therefore, relation (8) gives us the possibility of interpreting the gigantic frequency factor without hypothesizing an excessively large effective cross section Φ_{ex}. /80

An even more favorable situation appears if we assume, instead of the thermostimulated transition, an optical 2-1-transition, and a lifetime of the excited state of $\tau_2 \gg 10^{-8}$. But here the excited state must not be a 2p

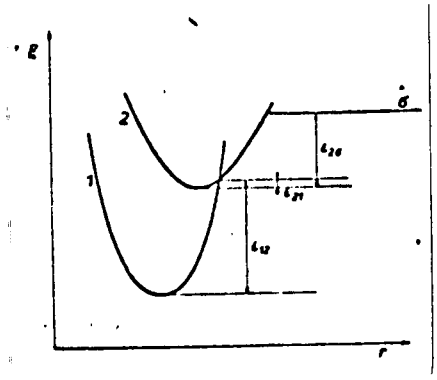

Figure 3. The Frank-Condon scheme for relations in two-stage excitation of the center electrons.

state, because the probability of the optical transition would be too small in comparison to that of the thermal transition. We have not yet been able to demonstrate the existence of such an optical transition.

One of the most important questions in the desired interpretation is the source of the monomolecular process. That is, we must take into consideration the fact that the effective cross section for anion vacancies for the capture of electrons is comparable to, or even large in relation to, that of the quasi-neutral defect electron centers, with which the electrons liberated from the F-centers recombine. Under these conditions one can hardly expect monomolecularity of the decolorization process without the decay of the anion vacancies left by the electrons. But, as is well-known from experiments on the coloring of NaCl by x-radiation, the concentration of the disperse anion vacancies in the crystal is too small to produce a measurable coloring. Individual vacancies are only set free by radiation. In the decolorization process, therefore, the anion vacancies freed of electrons must in some way condense again. If this condensation is rapid enough, then there is never a large enough concentration of anion vacancies so that recapture of electrons would be expressed.

Therefore, fulfillment of the condition

$$\tau_{\square^-} \ll \tau_{eF} \tag{10}$$

is decisive for the origin of the monomolecular process. Here $\tau_{\square^-}$ is the mean lifetime of the free anion vacancies, and τ_{eF} is the mean lifetime of the mobile electrons in relation to the captured ones. Knowledge which is

available so far does not, unfortunately, allow us to confirm the validity of (10). But it can be assumed, because if we neglect scattering, we have for $\tau_{\sigma F}$ /81

$$\tau_{\sigma F} = \frac{1}{v_\sigma \Phi n_{\square -}} \tag{11}$$

where v_σ is the mean velocity of the movable electrons, Φ is the effective cross section of the anion vacancy for capture of electrons, and $n_{\square}$ is the concentration of free vacancies. Therefore, $\tau_{\sigma F}$ is strongly dependent on $n_{\square}$. It can assume large values as $n_{\square -} \to 0$. On the other hand, the value of $\tau_{\square -}$ remains limited by the condensation of free vacancies at the surface of the crystal. If scattering is not negligible, the situation is even more favorable.

For interpreting the nature of the decolorization process, the following facts are of decisive importance: 1. The electrons freed from the F-centers pass through a higher energy state, as the exoelectron emission curves testify. 2. All the F-centers are decolorized in the high temperature decolorization process studied. At higher temperatures, no F-centers are capable of existing, and they disintegrate rapidly.

The interpretation considered is compatible with both these facts.

Now let us consider the problem of the second interpretation, according to which the decolorization is the result of a reaction between lattice defects. The basic concepts of this view were formulated in [11].

Of all the possible reactions, we consider only those in which a monomolecularity of the decolorization process can result. Thus, we must exclude reactions between the F-centers and the defect electron centers, because monomolecularity requires an excess of the partners reacting with the F-centers. Since the decolorization process goes on particularly in pure NaCl, it is

probable that the reaction partners of the F-centers can be nothing other than the cation vacancies, and the surface of the crystal serves not only as a source, but also as a trap for the reaction partners. This would insure the inexhaustibility of the source and trap required on the basis of monomolecularity. But at the same time it is difficult to explain the large frequency factor without introducing the hypothesis of a gigantic effective cross section of the F-centers for the reaction with the cation vacancy.

Zaitov et al. [8, 15], although they erroneously gave a simple explanation for the large frequency factor, have in practice without exception established only small frequency factors and have not concerned themselves further with this problem.

On the other hand, the value established for the thermal activation energy is of interest from the viewpoint of this interpretation. According to this model,

$$\varepsilon = \varepsilon_{\square-} + \varepsilon_r - \varepsilon_f \tag{12}$$

where $\varepsilon_{\square-}$ is the energy necessary to produce a cation vacancy, ε_r is that needed to produce the reaction, and ε_f that needed to destroy the cation vacancy. If we postulate that both ε_r and ε_f are approximately equal to the energy required to jump across the vacancy, then /82

$$\varepsilon \cong \varepsilon_{\square-} \tag{13}$$

According to [16], the energy needed to produce a vacancy pair in NaCl is 2.02 eV, which agrees well with the value of ε which we have determined.

A hybrid process would also be reasonable. That is, a center of another type is first produced by reaction between lattice defects, and it is then thermally ionized [17].

Obviously, with the difficulty of obtaining decisive experimental material in this view, it is difficult to say anything definite about this problem.

But there is still one more argument which supports the first interpretation. This is the result of Smakula [4]. He worked with monocrystals electrolytically additively colored, and established approximately half of the value that we found for the activation energy. This can easily be explained by thermodynamic equilibrium among the electrons in the centers and in the conduction band. The small shift toward smaller values can be ascribed to the exponential dependence of the scattering of the electron motion in the conduction band. If one wished to explain Smakula's results on the basis of the reaction mechanism, then one would have to suppose that under Smakula's experimental conditions either the energy required to produce the reaction partners dropped strongly, or the energy needed for their destruction increased strongly. But at this time we can find no basis for these hypotheses.

4. Conclusions

In the three parts of this work, we have investigated the thermal decolorization of F-centers in NaCl by means of exoelectron emission, luminescence, and optical absorption. We have established that:

1. With proper inclusion of the emission conditions for the emitted electrons, exoelectron emission can serve as a quantitative method for studying color centers.

2. The correct value for the thermal activation energy of the high temperature process destroying the centers is approximately 2.1 eV. We have verified this from several viewpoints.

3. The nature of this activation energy can be interpreted in different ways. The results which are known at this time substantiate the assumption that it is true thermal ionization energy of the F-centers, and not the other possible interpretations.

4. The decrease of the effective thermal activation energy of the delocalization process for the color center electrons to one half its value in the change from photochemically to additively colored crystals can serve as a proof of a thermal ionization of the color centers. /83

5. The relation derived by Albert Rose between the effective cross section of the capture centers and the frequency factor of thermal excitation is not generally valid. It represents nothing other than the statistical hypothesis on the equality of a priori probabilities of quantum states.

6. The explanation of the gigantic frequency factor for thermal destruction of the F-centers in NaCl is probably to be sought in a two-stage activation process.

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