User's Manual

STUDY OF THERMOLUMINESCENCE OF F-CENTERS IN ALKALI HALIDES CRYSTALS

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FIG. 2_ SCHEMATIC REPRESENTATION OF COLOR CENTERFORMATION AND DESTRCUTIVE

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INTRODUCTION

The elegant and fundamental research, which R.W. Phol at Gottengen initiated, has provided the experimental foundation for most of the subsequent work in this field. It is to Phol that we owe the term 'color centers' which is applied to the special electronic configuration in a solid that give rise to optical absorption in a normally transparent spectral region. With the recognition of the highly important influence of structural imperfections on the physical properties of solids, it seemed clear that imperfection were involved in the production and constitution of the color centers. As early as 1937 de Boer proposed a model for one of the color centers in the alkali halides (the 'F' center), which consisted essentially of an electron trapped at the position of a missing halogen ion (halogen ion vacancy). This model has survived the test of further theoretical and experimental investigation. Specific models of other color centers in alkali halides were later proposed, principally by Seitz, which like-wise involved electron or electron-deficiencies "Positive holes" trapped at aggregates of positive and negative ion vacancies.

Pure alkali halide crystals, which are transparent throughout the visible region of the spectrum, may be colored in a number of ways:

- (a) by the introduction of chemical impurities
- (b) by introducing an excess of metal ions
- (c) by X ray, γ ray, neutron and electron bombardment
- (d) by electrolysis

COLOR CENTERS PRODUCED BY IRRADIATION WITH X-RAYS

When a crystal is irradiated with x-rays, electrons are stripped from some of the normal ions of the crystal. Thus equal number of electrons and positive holes are formed. Most of the electron quickly recombine with the holes, that is, the electron fall back into the stripped ions and reconstitute the normal ions. If, before this happens, a free electron wanders near an interstitial cation (or near an anion vacancy, or near a substitutional impurity cation of higher valancy than the lattice cations), this positively-charged defect can trap the electron in its coulomb field. The positive holes that escape early annihilation also wander through the crystal and are trapped at negatively charged defects, such as cation vacancies. Fig. 1 shows different ways of representing the neutral center (F-center) formed by the trapping of an electron at a negative ion vacancy in an alkali halide.

Trapped-electron or trapped hole centers formed by such means as X-irradiation of a crystal can be destroyed (bleached) by warming the crystal or by illuminating it with light of the appropriate wavelength. This is readily understandable in view of the fact that an electron trapped by a positively-charged defect comprises a system analogous to a hydrogen atom. As such it has various excited states into which it can be excited thermally or by absorption of light of the requisite energy. With the absorption of sufficient energy, the electron can be completely freed from the defect, paralleling the ionization of a hydrogen atom. If the free electron encounters a trapped positive hole during its migration through the crystal, it can fall into the hole and annihilate it. The same considerations apply to the ionization of a trapped-hole center, following which the free hole encounters a trapped electron and is annihilated. These processes of forming and bleaching trapped-electron and trapped hole centers are represented in the band picture as shown in Fig. 2.

TRAPPED ELECTRON AND PHONONS

Let us consider the interaction between trapped electrons and phonons - as example of these interactions, we shall discuss the electronic excitation due to the thermal vibration in crystals.

(a) The Adiabatic Approximation and the Frank-Condon Principle

The Hamiltonian of the total system of the electron under consideration and atoms constituting the crystal is expressed by

 $H(r,Q) = H_e(r) + H_1(Q) + H_{e1}(r,Q)$

Here r is the coordinate of the electron and Q represents the coordinates of each atom. The first term on the right-hand side of the equation express the energy depending on the coordinate of the electron only, the second term the energy depending on the coordinates of lattice points only, and the third term is the interaction term. It is well known as in the cases of molecules that the wave equation associated with the Hamiltonian of Eq. (1) can be solved in the adiabatic approximation in which the fact that the electron mass is very small compared with that of the crystal atoms is used. The wave equation is separated into two parts:

$$\left[H_{e}(\mathbf{r}) + H_{e_{1}}(\mathbf{r}, \mathbf{Q}) \right] \boldsymbol{\theta}_{n}(\mathbf{r}, \mathbf{Q}) = E_{n}(\mathbf{Q}) \boldsymbol{\theta}_{n}(\mathbf{r}, \mathbf{Q})$$
(2)

and

$$[H_{1}(Q) + E_{n}(Q)]\zeta_{nv}(Q) = W_{nv}\zeta_{nv}(Q)$$
(3)

the wave function ψ of the total system being

$$\Psi_{nv}(\mathbf{r}, \mathbf{Q}) = \boldsymbol{\theta}_{n}(\mathbf{r}, \mathbf{Q}) \boldsymbol{\zeta}_{nv}(\mathbf{Q})$$
(4)

Eq.(2) is the wave equation used to calculate the electron energy, taking Q as parameter.

Fig. 3 shows a schematic diagram for adiabatic potentials, taking Q as one- dimensional. Since Q is not changed, according to Frank-Condon principle when an electron is transferred from the ground electronic state to an excited electronic state by absorption of light, the energy corresponding to the peak of the absorption band is equal to the magnitude of $A \rightarrow B$ in the figure. This excited electron either goes back to the ground state by emitting light with the probability of the spontaneous radiation or is transferred to the state C in the figure by giving up energy as phonons. If the latter, process occurs with very large probability compared to the former, the energy corresponding to the peak of the emission spectrum is equal to the magnitude of $C \rightarrow D$ in the figure. If there is forbidden transition state among the excited states which is slightly lower than an allowed-transition state, the specimen is a luminescent material with long residual light property, storing the energy of the light for a long time, since an electron in the original excited state may be transferred to the forbidden-transition state by emitting long wave-length light or by giving up the corresponding energy to a phonon (see Fig. 4).

(b) Thermal excitation of trapped electrons

As an example of the phenomena described by the Hamiltonian of Eq. (1) we shall study the thermal excitation of a trapped electron by phonons and as a special case, the ionization of the electron, producing a conduction electron.

We shall qualitatively discuss the probability of this process to occur using Fig. 3. It is easily conceivable that for the system in the ground state to transfer to an excited state it is necessary that the system in the ground state have energy close to the energy of point G. However, if there is an excited state which has the same energy as the system in the ground state such a transition as $G \rightarrow C$ of the figure may be possible by the quantum mechanical *tunneling effect* through the adiabatic potential well. The probability of this transition depends on the potential well GFC. Therefore, if the probability of the system being in the state F of high energy is large because of rising temperature, the transition is mainly due to an *activated process* for going over the potential hill. In either case the probability per unit time is expected to be given by

$$P = \beta_0 \exp\left(-E / kT\right)$$
(5)

Here β_0 is a coefficient whose contents can be determined by extensive quantum mechanical consideration of the process. The value E is the E₀ of Fig. 3 if the transition is controlled mainly by the tunnel effect while E is E^{*} if the activated process is the main cause for the transition. As an example of experiments to observe these processes we shall take the *thermoluminescence* of luminescent materials.

For simplicity we shall consider active centers in a luminescent material whose adiabatic potentials are in the form of Fig. 4. An electron trapped in the ground state is excited by absorption of light and soon goes from the state C to the *metastable* state A by either emitting light or interacting with phonons. If it is forbidden to return to the ground state from the state A by emitting light this center "stores" light, imparting a long residual glow to the crystal. Let us assume that the cause of the residual glow is in fact that the electron in the state A goes to the excited state by a phonon collision, and then emits the light from the state C. Assume further that the probability of this emission is much larger than that of Eq. (5) for thermal excitation from A to C. Then, the characteristic time of the residual glow, i.e. the number of photons, I, emitted per unit time is governed by the thermal excitation process and is given by

$$I = -\frac{dn}{dt} = np$$
(6)

where n is the number of active centers which have their trapped electron in the metastable state. Integrating Eq. (6) we get

$$\mathbf{I} = \mathbf{n}_0 \,\mathbf{P} \exp\left(-\mathbf{p}\mathbf{t}\right) \tag{7}$$

where n_0 is the value of n at t = 0. Since I is decreasing exponentially we obtain P when we find the attenuation constant from the observation of the time dependence of I. When we plot log P with respect to 1/T by performing this experiment for various temperatures the result will be a straight line provided Eq. (5) is correct, and from the slope of the straight line we can obtain the *activation energy* E. From the log P value obtained in the limit 1/T = 0, we can find B₀. KCl - TI crystals are examples for which the above considerations fit very well. It is observed that the activation energy E is 0.67 eV and 0.51 eV for KCl - TI and KI - TI, respectively, and the β_0 are respectively 2.9x10⁹sec⁻¹ and 2.1x10¹²sec⁻¹. Fig. 5 is an experimental verification of the straight line relation mentioned before.

In most experiments, however, a glow curve is drawn because of its simplicity. In this method the time dependence of the intensity of emitted light is observed while a specimen in a state of "light storage" is slowly heated at a constant rate. If we denote by $\beta = \frac{dT}{dt}$ the constant heating rate, we obtain by integrating Eq. (6)

$$\log_{e}\left(\frac{n}{n_{0}}\right) = -\int_{0}^{T} \frac{P}{\beta} dT$$
(8)

and hence obtain

$$I(T) = n_0 p \exp\left[-\int_0^T \frac{p}{\beta} dT\right]$$
(9)

Fig. 6 shows the good agreement (for a KI - T1 crystal) between observed values and the theoretical result which a plot of Eq. (9) is using the E and B_0 obtained from Fig.5. This curve is called a glow curve. From the temperature T_G of the peak of the curve we can estimate the activation energy E approximately by

$$E = k T_{G} \ln\left(\frac{\beta_{0} T_{G}}{\beta}\right)$$
(10)

Since this value is not so sensitive to β_0 , by substituting $10^{10} - 10^{12} \text{ sec}^{-1}$ for β_0 , we may obtain a crude estimate of E. If the specimen contains different kinds of active centers with similar properties there appear many peaks on the glow curve at various temperatures, each being associated with the activation energy of a specific kind of center. This experiment is a useful method of studying the energy states of a trapped electron.

DESCRIPTION OF THE APPARATUS

- 1. Alkali Halide Crystal: The KCl or KBr crystal is supplied with the apparatus. This may be pasted with araldite on the tip of the sample holder (a brass rod) mounted in the lid of the oven, facing the window. The crystal with its stand can be taken out for irradiation by X-ray.
- 2. Oven: This is a small oven for heating the crystal upto 423K (150°C) with RTD sensor.
- **3.** Thermoluminescence Temperature Meter, Model TL-02: It has a Power Supply for the oven and a digital temperature meter to read the temperature of oven directly in K. Since the RTD (housed in oven) is fast response sensor, the temperature of the crystal can be measured accurately and conveniently. This is particularly important when the temperature is rising at about 10-12K/minute.

4. Photomultiplier Tube, its Housing and Biasing Circuit:

- (a) <u>Photomultiplier Tube</u>: Generally, 931-A tube is used but IP 21 & IP 28 tubes are equally good. Response of these tubes is in the range of 3000A° 6500A° with a maxima at about 4200 A°. Over-all voltage requirement is about 800 900 V d.c.
- (b) <u>PMT Housing</u>: The housing is made of thick soft iron to provide a shielding from stray light. The shutter arrangement at the window is provided to adjust the size of window according to incident beam and to protect the photomultiplier tube from light when not in use. For E.H.T. input and photomultiplier output, amphenol connectors are provided.
- (c) <u>Biasing Circuit</u>: A general purpose biasing circuit is mounted into the base of the PMT Housing.

For more details of photomultiplier, biasing circuit etc. please see our booklet on 'Photomultipliers'.

5. High Voltage Power Supply, EHT-11: This is a fully solid state power supply designed to meet the power requirements of broad range of radiation detectors.

Output : 0 - 1500 V continuously adjustable.

Current : 1 mA (max.)

Polarity : Negative

Regulation : $\pm 0.05\%$

Display : 3¹/₂ digit 7 segment LCD with autopolarity.

For detailed specifications, and operational instructions please see our manual on 'High Voltage Power Supply, EHT-11.

6. Digital Nanoammeter, DNM-121: This is very versatile and general purpose instrument. The unit is specially suited for the measurements in the range of $100 \,\mu$ A to $100 \,p$ A.

Range	: 100 nA, 1 μA, 10 μA & 100 μA with 100% overanging.
Input	: + ve or -ve d.c.
Accuracy	: 0.25%
Display	: 3 ¹ / ₂ digits, 7 segment, LCD with autopolarity and decimal indication.

For detailed specifications and operational instructions, please see our manual on Digital Nanoammeter, DNM-121.

7. Black Box: This is for housing the oven with its stand and photomultiplier with its housing & biasing circuit etc. There are provisions for shielded cables for EHT Power Supply, Nanoammeter and leads for the oven. The box can be opened and closed with two sliding type shutters. The experiment can be performed without a dark room. As an additional precaution, the black box may be covered with thick black cloth provided with the black box.

EXPERIMENTAL PROCEDURE

- 1. Remove the cover of the PMT Housing and insert the photomultiplier tube gently in its base in a dim light. The PMT should not be exposed to strong light. Put back the cover and fix it with the help of two screws. Make sure that the shutters of the PMT Housing are closed.
- 2. Connect the coaxial cables with EHT and Nanoammeter and the 3 pin power plug to ovens power supply.
- 3. Put the small oven on its stand and made sure that the window of the oven is properly aligned with the window of the PMT Housing.

- 4. Take out the lid of the oven and insert the sample holder. Make sure that these can be inserted or taken out smoothly. Take the sample holder and put back the cover of the oven.
- 5. Close the black box with the help of two shutters provided. The shutters of the PMT Housing should also remain closed.
- 6. Connect the EHT Power Supply and Nanoammeter to 3 pin main's sockets. A good earth point is absolutely essential for their proper functioning. Let the whole system stabilize for about one hour, if the tube is inserted for the first time and about 20 30 minutes in normal use. The system is now ready for the measurement of very weak intensities.
- 7. Put the sample holder mounted with the alkali halide crystal as near the x-ray window as possible and switch on the x-rays. Normally 5 15 minutes of exposure is enough, depending upon the intensity of x-rays. The whole of crystal should be colored. The colour will depend upon the material of the crystal.
- 8. Insert the sample holder in its place such that its top is flushed with its hole. This would make the position of the crystal in the center of window. The flat face of the crystal should face the PMT window. In case of new crystal this position should be suitable marked on the stand. Open the PMT Housing window and close the black-box.

Note: Switch off the EHT supply before the black box is opened for inserting the crystal. The Nanoammeter may remain 'ON'.

- 9. Switch on the EHT and increase the voltage gradually to about 800 volts.
- 10. Let the system get stabilized for about 5 minutes if the EHT and Nanoammeter were ON before hand or to 15 20 minutes otherwise.
- 11. Select the appropriate range (say 100nA) of the Nanoammeter.
- 12. Connect the oven with TL-02 and switch on the oven.
- 13. Take the observations of intensity (output of photomultiplier tube in nA) vs. temperature. To obtain the rate of heating (°C/sec), take a initial reading of time at about 10°C above room temperature and another near the T_G (the temperature corresponding to the peak of the curve). A typical glow curve for KCl crystal is given in Fig. 7.

CALCULATIONS

From equation (10), the activation energy (E) is given by

$$\mathbf{E} = \mathbf{k} \, \mathbf{T}_{\mathrm{G}} \, \ln\!\left(\frac{\beta_0 \, \mathbf{T}_{\mathrm{G}}}{\beta}\right)$$

Where,

- k is the Boltzmann constant ($8.6 \times 10^{-5} \text{ eV} / \text{K}$)
- T_G is the temperature corresponding to the peak of the curve (363 K).
- β is the rate of heating 13×10^{-2} deg / sec.
- β_0 is the quantum mechanical constant for the system (generally in the range of 10^{10} 10^{12} . Since E is not very sensitive to this factor, we take it as 10^{11}

$$E = (8.6 \times 10^{-5}) \times 363 \times 2.3026 \text{ Log}_{10} \frac{10^{11} \times 363}{0.13} = 1.04 \text{ eV}$$

PRECAUTIONS

- 1. Please read the instrument manuals on 'High Voltage Power Supply, EHT-11', 'Nanoammeter DNM-121' and 'Photomultipliers' supplied with the set-up, very carefully and handle these instruments accordingly.
- 2. A good earth point and mains voltage in the range of $220 \pm 10\%$ are absolutely essential for the proper functioning of the system.
- 3. The photomultiplier tube exposed to strong light may result in permanent damage. It should be handled in dim light only. The black box should not be open while H.T. is on this may also result in damaging the tube. Keep the PMT Housing shutters closed when not in use. To avoid stray light, a dim light in the room is desirable. The thermometer lower part is covered with a copper sheath to avoid stray light through the thermometer.
- 4. For irradiation of the crystal mount the crystal on suitable stand. X-rays are very harmful and its exposure should be avoided at all cost.
- 5. In case the coloured crystal is to be stored for some time, it should be covered with black paper or store in dark place. Never touch the crystal with fingers as this may damage and contaminate the surface.
- 6. A heating rate of about 5 to 8°C per minute is recommended.
- After the experiment is over, switch off the EHT, Nanoammeter & Oven Power Supply. Remove the cover of the black- box and close the shutters of PMT Housing. This would avoid the unnecessary of the PMT.

REFERENCE

- 1. Solid State Physics by Kubo and Magamiya (McGraw-Hill).
- 2. International Series of Monographs on Solid State Physics Vol.2 (Color Centers in Solid by Schulman and Compton, Pergamon Press).