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Publication Date
1962-10-09
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Berkeley, California
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THE EFFECT OF HYDROSTATIC PRESSURE
ON THE LOW-TEMPERATURE THERMOLUMINESCENCE OF NaCl

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(M. S. Thesis)

October 9, 1962
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THE EFFECTS OF HYDROSTATIC PRESSURE ON THE LOW-TEMPERATURE THERMOLUMINESCENCE OF NaCl

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October 9, 1962

ABSTRACT

The effect of hydrostatic pressures up to 10,620 atmospheres on the low-temperature glow curve of NaCl is measured. It is found that one glow peak is enhanced by pressure in the range of conditions studied. It is proposed that this enhancement is caused by the production and movement of dislocations within the crystal lattice. This movement creates vacancies and interstitials which will affect the luminescence.

The experimental procedure consists of irradiating single crystals of NaCl with a cobalt-60 source at liquid nitrogen temperature. After irradiation, the crystal is heated and the subsequent glow is recorded by a photomultiplier tube. The crystal is then pressed hydrostatically for a period of time, and the above procedure is repeated. A comparison is made between the glow curves obtained before and after pressing the crystal to determine what effect pressure has on the luminescence.
I. INTRODUCTION

A. Thermoluminescence, General

If a crystalline substance is irradiated at low temperatures and subsequently heated, luminescence may occur. This glow is called thermoluminescence because the thermal energy absorbed as the substance warms up releases the glow near a certain temperature. This temperature is characteristic of the substance and is affected by the warming rate, the radiation dose, and certain types of pretreatment given the crystal. The mechanism of thermoluminescence is thought to be one in which electrons are excited from a bound state into a conduction band by ionizing radiation. In the conduction band they migrate through the crystal until they reach a trapping site. An imperfection in the crystal lattice at which a negative ion is missing is such a site. If the electron "substitutes" for the negative ion, it is held in this position, which is now referred to as an F center. If this electron receives sufficient energy to break away from the F center and re-enter the conduction band, it can decay to some ground state with the emission of heat or light. If light is emitted, the process is termed luminescence. If thermal energy releases the trapped electron from the F center upon heating of the substance, the glow is called thermoluminescence.

In addition to F centers there are several other types of trapping sites thought to contribute to the luminescent process. For a discussion of the various types of centers see the paper by Seitz.

Thermoluminescence may be divided into two categories, a high-temperature and a low-temperature glow. The former is that glow curve obtained above room temperature, and the latter is that obtained below room temperature. In particular, this paper is concerned with the low-temperature thermoluminescence from 77 to $300^\circ$K.
B. Factors Affecting Luminescence

The history of a sample may have a marked effect on its luminescent properties. Doping a sample with impurities can affect its thermoluminescence. Impurities may take up interstitial positions and may enhance or quench luminosity. For instance, nickel and iron impurities suppress luminescence from certain phosphors, whereas excess sodium in NaCl enhances certain portions of the glow.

Heat pretreatment also has an effect on luminescence. It is thought there are at least three different mechanisms at work during preheating. These are (a) diffusion of oxygen into the crystal which may act as a luminescent center, (b) production of vacancies on the surface of the crystal, and (c) migration of surface vacancies into the interior of the crystal and redistribution of the inner vacancies. Halperin and co-workers found that thermal pretreatment of NaCl in the air at 550°C greatly enhances the low-temperature glow. In addition to this effect they found that "the peaks at higher temperatures undergo a drop in intensity, which is stronger the higher the peak temperature."

Halperin suggests there may be a diffusion of oxygen into the crystal and a migration of holes and positive-ion vacancies through the crystal during preheating such that low-temperature thermoluminescence is strongly enhanced and high-temperature thermoluminescence is suppressed.

Concerning the latter mechanism he theorizes that (a) holes and positive-ion vacancies produced by heating diffuse from the surface of the crystal into the interior, and (b) holes and vacancies inside the crystal diffuse into a more even distribution. In support of (a) Halperin found that heating NaCl in a sodium atmosphere caused certain low-temperature peaks and all the peaks above room temperature to disappear. This disappearance is explainable in terms of the diffusion of sodium atoms into vacancies in the crystal lattice that were produced by heating. If one attributes the high-temperature peaks to the migration of carriers to nonneighboring recombination centers, these peaks should be less intense if centers migrate within the crystal during heat pretreatment. The fact that the high-temperature peaks do decrease in intensity upon heat pretreatment may lend support to (b) above.
To determine what role is played by the atmosphere, Spicer pre-heated NaCl in both air and vacuum and found that "essentially the same results were obtained whether the crystals were heated in air or in vacuum down to $10^{-5}$ mm Hg." From this result it may be assumed that diffusion of oxygen into the crystal during heating does not play a role in changing the luminescent properties.

Bonissoni et al. performed similar experiments on KCl. Heat pretreatment in air was found to enhance the glow. To determine the role played by the air, Bonissoni heated KCl in a vacuum and found a marked absence of any luminescence. About this finding he concludes, "From our observation of the absence of luminescence in KCl crystals annealed in vacuum, there seems to be little doubt that atoms of the ambient gas (probably oxygen), diffusing into the crystal play an essential role in the observed phenomena." Bonissoni acknowledges the results obtained with NaCl by Spicer, but he argues that the vacuum system used by Spicer may have been faulty. However, he also admits that NaCl and KCl may behave differently.

If we assume that the results obtained by Spicer and Bonissoni are valid, the work done on NaCl suggests that heat treatment produces vacancies on the surface of the crystal which then diffuse into the crystal. These vacancies are responsible for the marked increase in the luminescent intensity of the low-temperature peaks. The work on KCl suggests that diffusion of oxygen into the crystal is the contributing factor to the change in luminescent properties upon thermal pretreatment of this substance.

### C. Effects of Hydrostatic Pressure on Crystals

The observation that past history of a sample has a great effect on the glow curve of NaCl led to investigation of the effect of hydrostatic pressure on single crystals of NaCl. It is unlikely that hydrostatic pressure can produce holes or vacancies or cause migration of vacancies within the crystal. In fact, Lazarus has shown that the activation energy for motion of vacancies increases with pressure in NaCl." Under purely
hydrostatic conditions no change is expected to take place in the crystal structure, and therefore, the luminescent properties should not change. This effect has been observed by Kuppenheim.  

D. The Role of Dislocations in Luminescence

It is to be noted that hydrostatic pressure can exist only in a perfect crystal. In any real crystal, internal pressure gradients will be caused by gas or water bubbles, voids, and other defects present. Therefore, although the pressure on the surface of the crystal is hydrostatic, the pressure inside is not. The pressure gradients inside the lattice will increase with increasing external pressure, and at some point the gradient inside will exceed the local shear limit. Plastic flow will occur and the crystal structure will change. The most likely type of change will be the formation and movement of dislocation lines. The theory and description of dislocations are not discussed here, but the interested reader is referred to the book by Cottrell. Instead, some properties applicable to this work are discussed.

If stress is applied to a dislocation line which has its ends anchored, the line will deform and close on itself to form a loop. Continued stress will cause expansion of this loop. Stresses also may cause the displacement of certain types of dislocations, called edge and screw dislocations. It is reasonable that pressure gradients within the lattice can provide these stresses. When dislocations move through the lattice, they both generate and absorb vacant sites and produce interstitials. This effect changes the luminescent properties of the material.

As mentioned previously, hydrostatic pressure has the effect of immobilizing vacancies in the crystal. If it is reasonable to assume that pressure will create new vacancies and interstitials by the movement of dislocations, then this rearrangement of the lattice should be apparent in some changed luminescent property. But there will be no migration of vacancies; thus, any change can be attributed to the action of dislocations.
II. APPARATUS

A. Radiation Sources

The irradiation facility consists of two cobalt-60 gamma-ray sources, one of about 700 curies and the other of about 25 curies. In the larger source the cobalt is mounted in small brass pencils 1.50-in. long and 0.125-in. diam. Sixteen of these pencils are arranged vertically in a 4-in. circle surrounding the sample. The smaller source is of similar geometry except that it has 16 pencils on a 2.85-in. diam. The dose received by the sample per unit time in the large source is roughly twelve times that received in the smaller source.

B. Sample Holder, Recording Apparatus, and Press

The sample holder is shown in Fig. 1. It consists of a brass tube of 0.75-in. inside diam. and 4.375-in. long. The sample lies on the bottom of the tube. At the top of the tube there is a 1.625-in. teflon fitting which mates to the photomultiplier housing.

The recording apparatus consists of an RCA 1P28 photomultiplier (PM) tube, a brass PM tube housing, a 2-kV voltage supply, an electrometer-voltmeter, and a Leeds-Northrup X₁X₂ model-G type-S potentiometer strip-chart recorder. This chart recorder has an accuracy of 0.3% full scale. It has a dead band of 0.1% and there is no zero shift over continual use.

In addition to the above, a small nichrome resistance heater with a variac is used to control the warming rate, which is held close to 1°C per second.

The photomultiplier tube housing is all brass with a teflon adapter to fit the sample holder. We use O rings to make lighttight seals at the window end and the tube-socket end of the housing (see Fig. 2 for details).

The electrometer-voltmeter is manufactured by the E-H Company and is an E-H model 215-RL.

A Mettler type-B5 precision balance is used to weigh samples prior to making runs with them. Weights are taken to the nearest tenth of a milligram.

The hydrostatic press consists of a 0.375-in. steel cylinder with two pistons. The pistons are fitted with O rings and bronze keeper rings to form a seal (see Fig. 3 for details).
Fig. 1. Cross section of the sample holder.
Fig. 2. Cross section of photomultiplier and housing.
Fig. 3. Cross section of hydrostatic press.
III. EXPERIMENTAL PROCEDURE

Early in the work a survey was done on approximately 35 inorganic substances taken from reagent bottles. This survey showed that some substances glow strongly, some weakly, and some not at all. The ability to glow did not fit any consistent scheme. Samples taken from the same bottle and handled in the same manner occasionally showed striking variations. Therefore, it was decided to concentrate on a common salt whose properties were well known, which could be obtained easily and in high purity, and which was readily compressible. For these purposes NaCl was chosen.

NaCl samples used are cleaved from Harshaw Chemical Company crystals. No analysis was done on the crystals used. For an estimate of the impurity content in typical Harshaw crystals see the reference by Duerig and Markham. Each sample is weighed and a glow curve is obtained for each virgin crystal before it is pressed. The radiation dose given each sample on this first run is so small it has no effect on future runs. This fact was established by irradiating and warming one crystal three times. The temperatures of the glow peaks were within 50K of each other and the area under the curves was the same within experimental error. Samples were then hydrostatically pressed with pressures up to 10,620 atmospheres for periods of time up to 110 minutes. The fluid medium used is a saturated solution of NaCl prepared with distilled water and Baker & Adamson reagent-grade NaCl. An experimental difficulty arose in working with a saturated salt solution at 10,620 atmospheres. At this pressure the dihydrate of NaCl forms on the crystal and the surface flakes away. Approximately 15 crystals were pressed and tested. It was found that the mass loss was compensated for by the same percent loss in the area under the glow curve. The maximum loss of weight by any crystal was 7%.

After a sample is removed from the press, it is reweighed and then sealed in the brass sample holder. The sample holder is cooled down to liquid nitrogen temperature and then irradiated by a Co\(^{60}\) source. A typical absorbed dose is around 600 r. After the sample is irradiated
the photomultiplier tube is connected and the sample holder is placed in the heater. The rate of heating is kept approximately constant at 1°C per second by manually adjusting the variac voltage. The temperature range covered is from 77 to 290°K.

In earlier work the brass sample holder was not sealed against outside air while it was at liquid nitrogen temperature. It was found that after as little as 60 seconds as much as 1 cc of liquid oxygen had formed. Liquid oxygen inside the sample holder upsets the temperature control and has an unknown effect on the crystals. Since a typical experiment requires the sample to be at liquid nitrogen temperature for from 2 to 5 minutes, it became necessary to make an airtight seal on the tube, for which a screw-on cap and a Teflon gasket were used (see Fig. 1).

The temperature of the sample was not measured for each run. Instead, several calibration runs were made with a thermocouple touching the sample during a normal warming cycle. By this method the temperature could be estimated within 5°K over the range from 77°K to 290°K. A plot of temperature versus time is shown in Fig. 4.

The hydrostatic pressure to which each crystal was subjected was calculated from the force applied to the pressure chamber. This force was read from a gauge on the hand press used to compress the crystals.
Fig. 4. Glow curves of NaCl crystals irradiated 2 min in Co$^{60}$ source (600 r); (a) virgin crystal (300 mg); (b) crystal pressed at 10,620 atm for 45 min (275 mg); (c) crystal pressed at 10,620 atm for 110 min (166 mg).
IV. RESULTS

A. General

Hydrostatic pressure applied to single crystals of NaCl is found to strongly enhance an emission peak at 250°K. After a pressure pretreatment of 110 minutes at 10,620 atmospheres, the area is increased by a factor of 8 and the maximum intensity by a factor of 6 (see Fig. 4).

It will be noted that there are slight differences in temperature and size of the other peaks. These differences are the result of variations in the crystal masses and variations in the warming rates. The greater the crystal mass, the larger the glow peaks, with certain exceptions (see Fig. 4c). It should be mentioned that even though crystal (c), Fig. 4, is smaller than (a) and (b) by a factor of about two, the glow curve obtained on the virgin crystal was comparable in size to curve (a).

Slightly different timing in beginning each run causes small variations in warming rates. A difference in warming rates was also noted between small and large crystals. Both these factors can help explain why the maxima occur at slightly different temperatures, since different warming rates result in different peak temperatures.

B. Factors Investigated

Three areas of interest were investigated: (a) the effect of the duration of pressure on the glow; (b) the effect of delay between pressing and re-irradiating; and (c) the importance of the crystal surface.

There is an increase in luminescent intensity with increasing time of applied pressure. As seen in Fig. 4, the effect of 45 min pretreatment is slight compared with the effect of a 110-min press. This strong enhancement was obtained on three different crystals pressed for 110 min. The results obtained for crystals pressed for 10, 20, and 35 min, showed a very small increase in luminescence.

It was of some interest to determine whether the increase was a transient one or whether a permanent change had been made in the crystal structure. For this purpose one crystal was tested immediately after, 2 days after, 5 days after, and 7 days after removal from the press.
There was no decay of the 250°K peak over these periods, which indicated permanent damage had been done to the crystal.

One crystal that had been pressed was washed in water to determine if the effect observed was localized on the surface. The mass was reduced from 155 mg to 90 mg, but the size of the 250°K peak in relation to the rest of the curve was only slightly reduced. This result shows that the mechanism that changes the luminescent properties does not reside on the surface of the crystal.

C. Pressure vs Heat Pretreatment

It is of further interest to compare results shown in this paper with those of workers concerned with heat pretreatment of NaCl. In particular, Halperin provides much information for comparison. It is necessary to relate first the different sets of data. Halperin's peaks at 170 and 235°K correspond, respectively, to those at 200 and 250°K in this paper. The differences in temperature are explainable by differences in technique such as different warming rates and different radiation doses. Halperin presents three glow curves of interest here. First is that of a virgin crystal; second is that of a crystal preheated in air; and third is that of a crystal preheated in sodium vapor.

The curves of his virgin crystals are similar to the curves obtained in this paper with two exceptions. The relative intensities of the peaks are different, and this writer finds at least three peaks below 120°K which are absent in Halperin's work. The cause of the first discrepancy is unknown. Concerning the second, it is found that these low-temperature peaks decay with time at liquid nitrogen temperature and are absent after about 5 minutes. If Halperin delayed more than 5 min before warming the crystal, he would have missed these peaks. Delays in our work are of the order of 50 seconds.

More interesting are the curves of crystals preheated in air and in sodium vapor. These graphs are shown in Figs. 5 and 6. Attention will be devoted primarily to the peak at 235°K. (This peak corresponds to this paper's 250°K peak). Halperin's results show that it disappears
Fig. 5. (a) Virgin crystal of NaCl; (b) after 5 min; (c) after 44h of pretreatment at 550°C. (scale x 50). (See ref. 2.)
Fig. 6. (a) NaCl 45 min in air at 550° C; (b) after an additional 3.5 h in Na vapor. (See ref. 2.)
upon thermal pretreatment in sodium vapor. This observation indicates that the 235 K glow is not caused by interstitial Na atoms, but is probably a result of positive-ion vacancies in some arrangement or other inside the crystal.

As discussed in the introduction, heat treatment forms vacancies on the surface of the crystal. In addition, heat may cause movement of vacancies already inside the lattice and migration of vacancies from the surface to the interior. Since Halperin finds that heat pretreatment in air enhances the 235 K glow, this effect may be caused by the formation or movement (or both) of vacant sites. Since pressure pretreatment also enhances this peak, a similar mechanism is probably at work.
V. CONCLUSIONS

Our results show that hydrostatic pressure on single crystals of NaCl causes a permanent change in its crystal structure, which affects the luminescent properties. This change does not occur just at the surface but is effective throughout the lattice. Other evidence indicates that the change in luminescence is probably not caused by the formation of interstitials, but is probably a result of a change in the number or arrangement of vacant sites.

Since the effect of hydrostatic pressure is to immobilize vacancies, one is led to the reasonable conclusion that the change in luminescence is caused by the production of vacant sites.

Hydrostatic pressure may form dislocations inside the crystal. The movement of these dislocations generates vacancies and interstitials. The latter do not affect the glow peak studied. Instead, the result of hydrostatic pressure is to form vacancies which enhance the 250°K glow peak of NaCl.

It is interesting to speculate what practical applications our results may have. By proper choice of a material and sufficient pressure treatment, a dosimeter capable of reading doses down to 10 mr is probably possible. It is questionable whether or not NaCl is the best substance for this purpose.

The experimental method described here may be more useful in working with dislocations. In particular, these results may be valuable in studying the action of dislocations under conditions of very small strain. Much more work could be done in this direction with possibly very rewarding results.
ACKNOWLEDGMENTS

I would like to express my gratitude to those people at the Lawrence Radiation Laboratory who helped to make this work possible. I wish to thank Dr. Roger W. Wallace for his support and encouragement throughout the entire work. Dr. John Conway was particularly helpful in providing suggestions and advice whenever they were needed. In addition, I am indebted to Mr. Richard L. Lehman, who stimulated my interest in this field.

I should also mention the cooperation given me by Jim Byce, Chuck Krasel, and Duane Newhart, who helped design and build the apparatus.

This work was done under the auspices of the U. S. Atomic Energy Commission.
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Fig. 7. Small Co$^{60}$ source; (a) stationary stage holding sample; (b) movable stage with sources; (c) Co$^{60}$ pencils.
Fig. 8. Large Co\textsuperscript{60} source; (a) control boxes for moving lower stage; (b) empty Co\textsuperscript{60} pencil; (c) sample holder cup in lower stage; (d) Co\textsuperscript{60} pencils in stationary stage.
Fig. 9. Equipment during a warming cycle; (a) PM tube and housing; (b) nichrome resistance heater; (c) variac to control heater; (d) sample holder inside heater.
Fig. 10. Equipment arrangement during a run; (a) chart recorder; (b) high-voltage supply; (c) electrometer-voltmeter; (d) sample holder, PM tube housing, and heater.
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