Meetings and Conferences

CONFERENCE ON THE PHYSICS OF ALKALI-HALIDE CRYSTALS

F. KLEMENT and Ch. LUSHCHIK

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A conference was held in Tartu from the 30th June to the 4th July, 1959, on the physics of alkali-halide crystals; it was convened by the Scientific Committee on Luminescence of the Division of Physico-Mathematical Sciences, (U.S.S.R. Acad. Sci.), the Academy of Sciences of the Estonian S.S.R., and the Tartu State University. The conference united for the first time a wide circle of people working in various fields of solid state physics, such as crystallography, luminescence, dielectric properties, photoelectric phenomena, and mechanical properties.

Specialization in present-day science proceeds in the main in two directions: the different classes of phenomena, and the different classes of objects under investigation — the vehicles of these phenomena. It is obvious that an attempt to embrace the various phenomena in one viewpoint requires, at least in the first instance, the consideration of these phenomena in one class of material.

The crystals of the alkali-halide compounds are the classic object for investigating various properties of the solid state. This is explained by the simplicity of their chemical composition and crystalline structure, the relative ease of making large single crystals of them, and their ionic structure, which simplifies the consideration of the interaction between the particles of the crystal. Although normally dielectrics, they can reveal semiconducting properties after appropriate treatment (e.g., coloration). The optical, electrical and mechanical properties of these crystals have been studied in detail. In recent years the alkali-halide crystals have found wide practical use (scintillation counters of nuclear radiation, etc.). The alkali-halide crystals were the objects of the classical work of A. F. Ioffe, the school of R. Pohl, and the school of B. D. Kuznetsov and P. S. Tartakovskiĭ, which aimed some time ago at a parallel consideration of the different physical processes in these crystals. It is difficult to quote a more successful subject for the aims of the highly complex study of solid state physics. The phenomena occurring in a very complicated way in less simple substances can be studied in the alkali-halide crystals in the simplest model, in order to study them in the second or higher order of approximation in other systems. Also, it should be mentioned that the comparative simplicity of the alkali-halide crystals conceals the inexhaustible complexity of all the newly discovered properties and processes, and that even such a "well studied" object will remain the topic of long and careful investigations.

More than a hundred people took part in the Tartu Conference on the physics of the alkali-halide crystals. Amongst them were represented: Moscow [the Physical Institute and the Institute of Crystallography, (U.S.S.R. Acad. Sci.), the All-Union Institute of Mineral Raw Materials, et al.], Leningrad (the University, the Electrotechnical Institute, et al.), Tomsk (the Polytechnical Institute, the University), Khar'kov (Branch of the Inst. of Chem. Reagents et al.), Kiev (the University and Polytechnic Institute), Saratov (the University), Irkutsk (the University), Riga (the University and the Institute of Physics, Acad. Sci. Latv. S.S.R.) Baku (the Institute of Physics, Acad. Sci. Az. S.S.R.), Minsk (the Institute of Physics, Acad. Sci. B.S.S.R.), Lvov (the University), Alma-Ata (the Pedological Institute), Tartu (the Institute of Physics and Astronomy, Acad. Sci. Est. S.S.R. and the University). Even this list of towns and institutes shows how widely in our country work is carried on on the alkali-halide crystals, and how the necessity arose for uniting and coordinating it.

In all, thirty-six papers were presented; they can be tentatively grouped around three main problems:

1) Local states in crystals; luminescence and color centers.
2) Electron-hole and exciton processes.
3) Crystalline structure; ionic and dislocation processes.

Localized States in Crystals; Luminescence and Color Centers

In recent years it has been successfully shown that the alkali-halide crystals are crystalline systems containing various point and line (dislocations) intrinsic defects. Impurity ions are also distributed in crystals in accordance with the as yet poorly studied laws of "defect chemistry." Intrinsic and impurity defects and their simplest associations act as luminescent centers and capture centers for electrons and holes. Often, all these centers are called for short "impurity centers."

A large group of contributions to the Conference was devoted to the theoretical and experimental study of the nature of impurity centers in alkali-halide crystals, and to the study of the electron oscillator processes inside the centers.

The important contribution of **M. I. Petrashen'** (Leningrad), "Quantum-Mechanical Calculations of some Optical Properties of Impurity Centers in Crystals," was heard with interest. The principle ways of exact microscopic calculation on impurity centers of small radius, for which the macroscopic method of calculation developed by S. I. Pekar's school is inapplicable, were considered in the paper. The general methods developed by M. I. Petrashen' and his co-workers were used for calculating the optical characteristics of some actual centers in the alkali-halide crystals (F-center and luminescent center in KCl-Tl, the U-center), and for studying the spectroscopic laws in a homologous series of alkali-halide phosphors.

N. N. Kristoffel (Tartu) reported the results of a quantum-mechanical calculation carried out by him on the adiabatic potentials, and absorption and emission spectra of the luminescent center in KCl-Tl. The electronic transition $^1S_0 \rightleftharpoons {}^3P_1$ was considered in the Tl^+ ion, situated at a cation site and interacting with one fully symmetrical oscillation of the surrounding ions. Theoretical spectra were in good agreement with the experimental data.

The contribution of **I. V. Abarenkov** (Leningrad) was devoted to calculating the adiabatic potentials of the F-center in the polarized point lattice approximation. General expressions were also obtained for the moments of the spectrum of the impurity centers, taking into account the difference in the oscillations for the ground and excited states.

These three works completed the theoretical investigations reported at the Conference. Unfortunately, no report was given of the investigations by S. I. Pekar and his numerous co-workers, in which the theory of the alkali-halide crystals obtains its most complete and extensive development.

N. E. Lushchik and **Ch. B. Lushchik** (Tartu) devoted their paper to the spectroscopy of luminescent centers in alkali-halide crystals activated by a homologous series of impurity ions. It was shown that, in crystals containing "mercury-like" ions (Ga^+, Ge^{++}, In^+, Sn^{++}, Tl^+, Pb^{++}) and "noble" ions (Cu^+, Ag^+, Au^+), the basic energy and probability laws pertaining to the free ions are also qualitatively preserved for luminescent centers. It was thus proved spectroscopically that these ions are, in fact, "core" luminescent centers. In the paper were also considered some ways of predicting the spectra of phosphors from the known spectra of the free activated ions.

In the paper by **K. K. Schwartz** (Riga), the processes of quenching luminescence in alkali-halide crystals with "mercury-like" activators were discussed. It was shown that radiationless transitions inside a center, which cause thermal quenching of luminescence, take place in agreement with the ideas of Frenkel' and Mott. Optical quenching of the luminescence inside a center was not observed. The quantum yield of fluorescence does not depend on the frequency of the exciting light, not only in the Stokes region, but also in the anti-Stokes region. In the poly-activated phosphors KCl-Tl, Pb; NaCl-Pb, Mn and others, migration quenching of luminescence was studied.

I. K. Plyavin' (Riga) discussed the kinetics of short-lived photoluminescence in alkali-halide crystals. For phosphors containing Tl^+ ions, the lifetime τ in the excited ^3P state diminishes on increasing the temperature in the region of constant quantum efficiency. For phosphors activated by Ga^+ and In^+ ions $\tau(^3P)$ is practically independent of temperature. A theoretical interpretation of the results obtained was given on the basis of a model of the center with three levels (assumed to be $^1S_0$, $^3P_0$, and $^3P_1$).

J. J. Kirs and **A. A. Laisaar** (Tartu) studied the effect of hydrostatic pressure (up to 6000 atm) on the excitation and emission spectra of alkali-halide crystals activated by the ions In^+, Sn^{++}, Tl^+, Pb^{++}. Under pressure the excitation spectra of all the phosphors studied are displaced in the direction of lower frequencies, which indicates a decrease of the equilibrium configuration coordinates during excitation of the luminescent centers. The emission spectra change in a more complicated way. Their change is interpreted using a model of the center with two close excited levels.

The contribution by **T. A. Abdusadykov** (Alma-Ata) was concerned with the spectral characteristics of luminescent centers in alkali-halide crystals containing large concentrations of activator (In^+, Sn^{++}, Tl^+, Pb^{++} ions) and other defects of the crystalline lattice. In such phosphors there are luminescent centers of various sorts, differing from one another in the character of the nearest neighbors of the central "mercury-like" ion. The dependence of the number of complex centers on the number of intrinsic lattice defects shows that band defects of the basic substance probably enter into the composition of complicated centers.

The existence in singly-activated phosphors of activator luminescence centers of several types was also discussed in the paper by **A. F. Malyshevaya** (Tartu), who studied the spectra of crystal phosphors of the halogen salts of Group II metals with Tl^+ and Pb^{++} ions as activators. In the discussion **L. A. Rebane** reported a quadratic dependence of the number of complex luminescent centers in the phosphor NaCl-Ag on the activator concentration.

The role of intrinsic defects in ionic crystals as luminescent centers — widely studied in ZnS phosphors — has been little studied in alkali-halide crystals. A paper by **Z. L. Morgenshtern** (Moscow) was devoted to this interesting problem. The study of the luminescence from CsI crystals prepared under widely differing conditions, led Z. L. Morgenshtern to the conclusion that the emission band at $\lambda_m = 420$ mμ is associated with the presence in the crystal of microscopic defects of the vacancy type. Short wavelength luminescence ($\lambda_m = 350$ mμ) occurs in the more perfect crystals and can be tentatively assigned to emission of the pure lattice.

The detailed structure of many luminescence and color centers in the alkali-halides has remained unknown up till now. For the elucidation of this problem, polarization methods of study are very promising and have been applied with great success by P. P. Feofilov for studying the anisotropy of centers in cubic crystals.

The paper of **A. A. Kaplyanskii** (Leningrad) was of great interest: in it an original method for studying the anisotropy of the centers in cubic crystals was described, using the study of the splitting and polarization of the spectral bands under homogeneous elastic deformation by compression (extension). The method was successfully used for studying the sharp absorption and emission lines of LiF and also crystals of CaF_2-Eu^{3+} and CaF_2-Sm^{3+}.

The dichroism of colored alkali-halide crystals was treated in the paper by **O. A. Schmidt** (Riga). The question of the true and "artificial" anisotropy of centers, of some activator color centers, etc., was discussed. In the paper the theoretical basis was given of a method for determining the symmetry of centers in cubic crystals with the help of the linearly polarized photo-activation.

In the paper by **A. A. Shatalov** (Kiev), by generalizing the author's studies in recent years, the photochemical and thermal conversion of "defect centers" in additively colored alkali-halide crystals was examined from many angles. A series of experiments showed that the coagulation of F-centers takes place through the state of forming F_2-centers. The mechanism and kinetics of the reaction $2F \rightleftarrows F_2$ were studied in detail.

L. M. **Shamovskii** (Moscow), in his paper "On the Energy of Thermal Ionization of F-centers in Alkali-Halide Crystals," gave a critical analysis of the methods of determining the ionization energy of F-centers, based on the assumed presence in alkali-halide crystals of Frenkel' defects.

A. Kh. Khalilov, **É. Yu. Salaev**, **T. D. Alieva**, **A. P. Mamedov**, and **F. A. Isaev** (Baku) reported complicated investigations carried out by them on the spectra and thermal luminescence of NaCl, KCl, and KBr crystals exposed to x rays, and containing various cation and anion impurities.

Electron-Hole and Exciton Processes

Many of the electrical and optical properties of ionic crystals are directly connected with the migration through the crystal of charged and uncharged excitations which interact with the various defects of the crystalline lattice.

Particularly valuable data on electron-hole and exciton processes in alkali-halide crystals has been obtained from studies of the spectral variation of the external photoeffect yield. It was understandable, therefore, that the long paper by A. N. **Arsen'eva-Geil'** (Leningrad) — "The External Photo-effect from Alkali-Halide Crystals" — should be received with great interest. The paper provided a critical review of the main experimental and theoretical work in this subject, and original data was presented on the energy distribution of the electrons in the photo-effect from alkali-halide crystals containing F-centers.

The long paper by **Ch. B. Lushchik**, **G. G. Liid**, **I. V. Jaäk** and **E. S. Tiisler** (Tartu), was concerned with the role of electron-hole and exciton processes in the luminescence of Ga^{+}, Ge^{++}, In^{+}, Sn^{++}, Tl^{+}, Pb^{++} ions in alkali-halide crystals. Measurements of the excitation spectra and steady state luminescence and the excitation spectra of recombination phosphorescence in the alkali-halide phosphors showed that both charged and uncharged excitations participate in the transfer of energy from the host substance to the luminescence centers. In this process the efficiency of the electron-hole mechanism of transfer is greater than that of the exciton mechanism. Recombination luminescence is excited with particular efficiency in the region of the fundamental absorption bands, which have previously been tentatively ascribed to "band-band" transitions. The detailed mechanism of electron and hole recombination luminescence in ionic crystals was discussed in the paper.

In the paper by **I. V. Jaäk** (Tartu), the mechanism of the photo-thermal processes which lead to recombination luminescence and the formation of electronic color centers when crystals containing monovalent impurities are excited in the region of impurity center absorption bands was considered on the basis of data on the phosphorescence excitation spectra and "the creation spectra of color centers" in alkali-halide phosphors.

V. V. **Antonov-Romanovskii** described how the ionization of Eu^{++} in the phosphor Sr-Eu, Sm after photo-excitation was found in his laboratory by paramagnetic resonance.

G. G. **Liid** (Tartu) gave a paper describing an investigation of the dissociation and annihilation of excitons during interactions with defects in alkali-halide crystals. After illuminating KCl and KBr phosphors with ultra-violet light, which creates excitons, the formation of a series of electron and hole color centers (F, M, Z_1, V_1, V_2, etc.) was revealed by the straightforward absorption method. The luminescence effect of excitons on F-, R-, M-centers was studied in additively colored KCl and KBr crystals, and the interaction of excitons with monovalent and divalent mercury-like ions in KBr and KI crystals.

M. L. **Kats** (Saratov) devoted his paper to the changes of the absorption spectra of alkali-halides after exposure to ionizing radiation. Particular attention was paid to alkali-halide crystals containing heavy metal impurities. The activator ions are effective capture centers for electrons. Due to the localization of the electrons on the Ag^{+}, Cu^{+}, Sn^{++}, Ni^{++} ions, the absorption of light by these ions decreases and various "atomic" color centers arise.

The luminescence mechanism of atomic centers in the NaCl-Ni phosphor was the subject of the paper by **E. I. Shuraleva** (Irkutsk). It was shown that the luminescence occurring after exposure of NaCl-Ni to x rays is recombination luminescence.

More and more facts have accumulated in recent years indicating that the defects in alkali-halide crystals are distributed in a way very far from equilibrium. I. A. **Parfianovich** (Irkutsk), in his paper "On the Detailed Mechanism of Optical Flashes Stimulated from the F-band Region," presented interesting data on certain peculiarities of the flashes he has discovered, which provide evidence on how the electron and hole color centers in crystals exposed to x rays are distributed in "clusters." In the discussion on the paper there was mention of "the dichroism of optical flashes" discovered by **P. A. Khellenurme** in the region of the M-, N-, O-bands when the phosphor KCl-Tl is excited by light.

In the paper by **I. K. Vitol, Ch. B. Lushchik, I. V. Jaäk** and **M. A. Elango** (Riga, Tartu), consideration was given to the possibilities of the combined study of relaxation processes in alkali-halide crystals by optical, electrical and magnetic methods. The self-recording "relaxation combines" used in Riga and Tartu were briefly described; they permit simultaneous measurement of the non-isothermal relaxation of the absorption spectra, thermo-luminescence, and the stimulation spectra of optical flashes from previously excited crystals. The possibilities of the complex method were illustrated by a study of the mechanism of thermal destruction of color centers in alkali-halide crystals. In the discussion **P. A. Yurachkovskiĭ** described experiments he had performed to determine the activation energy of the thermal destruction process of F-centers in KCl.

The paper by **I. K. Vitol** (Riga), "The Photo-electric Properties of Defect-Gradient Layers in Alkali-Halide Crystals," was received with interest. Using the auto-compensating dynamic condenser method, the author studied the electrical polarization which occurs after illumination in the F-band or after heating, in uniformly colored crystals and in crystals having a thin layer at the surface which did not contain F-centers. The phenomenon of static polarization permits valuable data on relaxation processes in crystals to be obtained (especially on the sign of the optical and thermal charge carriers).

Crystalline Structure; Ionic and Dislocation Processes

Some idealization of the crystalline structure and the defects in ionic crystals was a characteristic of work in the first decade after the war. In recent years the number of investigations which take into account the complicated structure of real crystals has increased sharply. The progress has been particularly great in the study of linear defects of the crystalline lattice — dislocations. A special session at the Conference was devoted to the consideration of the effects associated with the presence in alkali-halide crystals of dislocations.

The paper by **M. V. Klassen-Neklyudova, G. B. Berezhkova, V. G. Govorkov, G. F. Dobrzhanskiĭ, V. L. Idenbom, V. G. Regel', G. E. Tomilovskiĭ, A. A. Urusovskaya** and **M. A. Chernysheva** (Moscow), attracted much interest; the work of The Laboratory for the Mechanical Properties of Crystals at the Institute of Crystallography, Acad. Sci. U.S.S.R., on the mechanical properties of alkali-halide crystals was summarized in it. In the first part of the paper, which was illustrated with exceptional clarity by cine-films, the various plastic properties of AgCl, LiF, CsI, CsBr and TlBr • TlI crystals were considered. In particular, the various phenomena of plastic deformation in crystals in homogeneous and inhomogeneous stress fields were treated (slip, irrational twinning, fracture). In the second part of the paper the results of studying the dislocation micromechanism of the phenomena observed were described. Particular attention was given to revealing the dislocations at the boundaries of mosaic blocks and slip lines in NaCl, AgCl, and LiF crystals by selective etching. The displacement of the dislocations by annealing and mechanical stress was studied and the effect of impurities on the dislocation mobility was considered.

L. M. Shamovskiĭ and **A. S. Shibanov** (Moscow) gave a paper entitled, "The Dislocation and Polyhedral Substructures in Crystals, and the Presence of Surface Active Impurities"; they communicated new data on the effect of impurities on the etch figures of KI crystals. The authors discovered a considerable increase in the density of etch pits in crystals containing activating impurities and reached conclusions on the preferential siting of impurities at dislocations.

A. A. Shatalov (Kiev) gave a paper on revealing lattice defects using additive coloring of alkali-halide crystals.

The paper by **R. Ya. Gindina** (Tartu) dealt with the decoration of defects in NaCl and KCl by non-isomorphic impurities. The choice of the annealing conditions for crystals activated by non-isomorphic impurities allows dislocations in the volume of the crystal and the dislocation net at the surface of the block structure to be decorated. Quenching destroys the decoration. The parallel investigation of absorption and luminescence in phosphors led the author to the conclusion that the commonly observed luminescence of alkali-halide phosphors is not connected with the luminescence from plane layers of activator sited at the block surfaces.

The results of x-ray analysis of the structure of alkali-halide crystals were communicated in the paper by **A. J. Pae** and **A. A. Haav** (Tartu). Analysis of Laue photographs from a large number of pure and activated alkali-halide crystals led the authors to conclude that the small amount of impurity in the melt is not the cause of the block structure in crystals, as revealed by splitting of the spots on Laue photographs.

O. G. Mankin and **N. E. Lushchik** (Tartu) communicated the results of a study by an absorption method of the diffusion of Ga^+, In^+, Sn^{++}, Cu^+, and Ag^+ ions in alkali-halide crystals from thin surface layers or from a gaseous phase. The speed of diffusion of Ga^+

and In^+ is comparable with the speed of self-diffusion. Cu^+ and Ag^+ ions diffuse several orders more rapidly. Here not only the usual bulk diffusion is observed, but also diffusion along dislocations.

L. M. Belyaev, **G. F. Dobrzhanskii**, **V. V. Chadaeva**, **V. P. Panova**, **Z. B. Perekalina** and **V. N. Varfolomeeva** (Moscow) contributed a paper, "Activated Crystals of Lithium Fluoride." The method of growing single crystals of LiF doped with magnesium, indium and uranium, was described in the paper, and their spectroscopic characteristics were discussed.

Interesting papers from the Tomsk school of physicists dealt with the study of the connection between the various optical, electrical, mechanical and other properties of the crystals and their composition. The physico-chemical properties of alkali-halide crystals were considered in the long paper by **A. A. Vorob'ev**, **P. A. Savintsev**, **V. E. Averichev**, **A. A. Botaki**, **V. Ya. Zelenko** and **M. N. Ignat'ev** (Tomsk). A relationship was established between the composition of NaCl • NaBr, KCl • KBr, NaBr • KBr, and KCl • RbCl solid solutions and their various physical properties. The hardness, Young's modulus, and electrical strength varied with composition, following curves with minima in the regions of intermediate concentrations; but the heats of formation, coefficients of linear expansion and dielectric losses followed curves with maxima in the same concentration regions. The greatest degree of imperfection of the crystalline lattice also occurs in the region of intermediate concentrations. Also discussed in the paper were the diffusion phenomena at the contact of alkali-halide single crystals.

The paper by **E. K. Zavadovskaya**, **M. S. Ivankina**, **I. Ya. Melik-Gaikazyan** and **M. N. Treskina** (Tomsk) was devoted to the effect of decay on the various physical properties of solid solutions. It was discovered that, on maintaining solid solutions for a long time, their defect content decreased; this was accompanied by an increase in density and in the coefficient of thermal conductivity, and a decrease in the electrical conductivity, etc. The effect of $PbCl_2$ impurity on the optical and electrical characteristics of KCl was treated in detail in the paper.

The concluding paper by **A. A. Vorob'ev**, **G. A. Vorob'ev**, **K. K. Sonchik**, **V. D. Kuchin**, **A. V. Astafurov** and **M. A. Mel'nikov** (Tomsk), provided a discussion of the results of extensive experimental research on the mechanism of electrical breakdown in alkali-halide crystals. The various ionization processes leading to breakdown were studied in detail, and it was shown that various electrical properties of the crystals are regularly related to the energy of the crystalline lattice.

The first attempt in the Soviet Union at an extensive conference on the physics of alkali-halide crystals can be considered a success. The participants at the conference — specialists in one narrow field or another — obtained ideas on the methods and results of representatives from neighboring specialized fields. The possibilities were revealed of using mutually, even at the present stage, the attainments of neighboring scientific areas; for example, luminescence methods in crystallography, and, vice versa, crystallographic methods in luminescence. Some papers also demonstrated that the simultaneous complex study of various physical processes in a single substance is already commencing in the confines of one laboratory (**A. A. Vorob'ev** — Tomsk, **Ch. B. Lushchik** — Tartu). At the same time the conference also revealed several inadequacies in the work being carried out. In the Soviet Union optical investigations of alkali-halide crystals are the most widely performed, photoelectrical studies are infrequent, and magnetic methods are very seldom used.

At the concluding session the participants at the conference expressed their satisfaction that it had been convened and the hope that similar conferences would be convened in the future.

The conference delegated to the Tartu physicists the preliminary work in this direction and the task of taking steps to coordinate scientific research in the physics of alkali-halide crystals.

Translated by K. F. Hulme