

COLOR CENTERS IN

THE Fourth International Symposium on Color Centers in Alkali Halides, held at the II Physikalisches Institut of the Technische Hochschule, Stuttgart, on August 21-24, 1962, attracted approximately 130 scientists from fifteen countries, with almost half of the attendance coming from the US.

The symposium, organized by H. Pick of the Institut with the assistance of a committee comprising H. Haken, F. Lüty, and H. C. Wolf, consisted of eleven sessions at which a total of eighty papers were presented dealing with the production of color centers by irradiation; the optical, electrical, and magnetic properties of color centers; impurity-type and impurity-induced color centers; the effects of deformation on coloration processes and color centers; exciton absorption and luminescence; and ionic transport phenomena in the alkali halides. In a brief address of welcome Prof. Pick noted the expansion of interest in color centers during the postwar years, recalled some of the events and personalities of earlier conferences, and paid special tribute to the pioneering efforts of K. Przibram and R. W. Pohl, whose presence made the Symposium particularly memorable.

The technical sessions began with an invited paper by F. Seitz, who reviewed the main features of present-day color center research, with emphasis on the extensive changes in viewpoint that have taken place within recent years. Up until about 1955 it was felt that color-center phenomena could be understood on the basis of the trapping of electrons or holes by negative or positive ion vacancies, respectively, or by aggregates of these defects. Thus, for example, since the *F* center had been established as an electron trapped at an anion vacancy, the *V_i* center was postulated to be a hole trapped at a cation vacancy, while the *M* center was postulated to be an electron trapped at an aggregate of two anion and one cation vacancies. These ideas were prompted by the fact that Schottky defects are the type most easily induced thermally in the alkali halides, and were fortified by an attractive and seemingly natural analogy between trapped-electron and trapped-hole color centers. The "structure sensitivity" of the coloration—i.e., its sensitivity to impurities and mechanical and thermal history of the sample—also seemed to find its natural explanation in this framework, which gave little emphasis to processes that could occur in the pure or ideal lattice, or to the possibility that interstitial ions or atoms could be involved in the constitution of color centers or in the mechanism of their formation. The proposal by Varley (1954) that vacancies and interstitial atoms could be formed by

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ALKALI HALIDES

By James H. Schulman



Among those who attended the international symposium in Stuttgart were honored participants K. Przibram and R. W. Pohl (above).

multiple ionization in the perfect lattice; Känzig's (1955) discovery of the *V_K* center, a Cl_2^- molecule-ion or self-trapped hole in the perfect lattice; Känzig and Woodruff's (1958) elucidation of the structure of the *H* center, essentially an interstitial chlorine atom; and Rabin and Klick's (1960) demonstration that low-temperature radiation coloration is an intrinsic property, not a structure-sensitive property of the crystal, required a considerable reorientation of color-center concepts.

The Stuttgart Symposium reflected the well-advanced state of this reorientation in many ways. V. Ritz (NRL) reported on studies of the energy dependence of the efficiency of *F* center formation by low-temperature irradiation, which supported the coloration mechanism proposed by Klick a few years ago, in which ionization of two adjacent halogen ions leads to the *F* center and *H* center formation, as opposed to mechanisms involving single ionization or multiple ionization of a single ion. D. Wiegand (Carnegie Tech) presented

observations that the fractional increase in lattice parameter produced by room-temperature irradiation is of the same order of magnitude as the fractional increase in linear dimensions, suggesting that interstitials are formed by irradiation at room temperature also. Further evidence for the formation of interstitial halide ions by irradiation was presented by F. E. Pretzel and R. L. Petty (Los Alamos), T. Hibi, K. Yada, and Y. Kawamata (Tohoku) described the complex pattern of structural changes observed electron-microscopically on electron or x-ray irradiation of single KCl crystals, which raised questions concerning the interpretation of linear expansion measurements or density-change measurements on irradiated alkali halides.

New methods for studying the mechanisms of coloration by radiation were described by J. W. Boag and J. H. Schulman (Mt. Vernon Hospital and ONR, London) and by D. M. J. Compton, P. H. Miller, and H. Schultz (General Dynamics/General Atomic), who employed microsecond pulses of electron beams to color alkali-halide crystals. The former investigators used flash spectroscopy to observe the room-temperature creation and decay of transient centers, predominantly of the trapped-hole type; while the latter studied the growth curves, self-bleaching, and rise time of the *F*-center absorption under pulse bombardment.

Van Doorn and Haven's (Phillips, Eindhoven) "double *F*-center" model of the *M* center, which was a controversial topic at the time of the Oregon Color Center Symposium in 1959, has been rather firmly established during the intervening years by the work of Van Doorn and by Faraday, Rabin, and Compton. At the Stuttgart Symposium attention was therefore given, not to the model itself, but to the mechanism whereby *F* centers aggregate to form *M* centers. E. Sonder (Oak

Ridge) reported that in KCl the $(M)/(F)^2$ ratio was specimen dependent and dependent on the intensity of the gamma or electron irradiation, but independent of the energy, in the case of electron irradiation. The $(M)/(F)^2$ ratio was completely reversible, so that a short irradiation at a new intensity level quickly established the $(M)/(F)^2$ ratio characteristic of the new dose rate. H. Rabin (NRL) discussed the thermal aggregation of *F* centers to form *M* centers, showing that the onset of migration of *F* centers to form higher aggregates begins at 207°K and increases rapidly with increase in temperature. He pointed out that, due to thermoluminescence from the various centers released during the warm-up of the crystal, the thermal aggregation of *F* centers in the "dark" may have the same underlying mechanism as the optical formation of *M* centers by bleaching in the *F* band.

Rabin also observed a band coincident with one of the absorptions attributed to a higher excited state of the *M* center. The existence of such absorption bands, particularly *M*-center absorption bands "hidden" under the *F* band, was postulated several years ago by van Doorn and Haven and was still a subject of disagreement at the 1959 symposium. Since that time Okamoto (Argonne) had found indirect evidence for several absorptions due to transitions to higher *M*-center states; Rabin's direct observation of one of these bands appeared to strengthen this analysis. Further evidence for the existence of absorptions due to *M* and *R* centers in the region of the *F* band was presented by K. G. Bansigir and E. E. Schneider (Newcastle upon Tyne), who found partially resolved peaks in the *F*-band region in x-rayed crystals which had been subjected to bleaching with polarized light under a shearing stress in the $\langle 110 \rangle$ directions. The observed dichroism of the vari-



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ous components was found to be compatible with the models of these "secondary" centers proposed by Pick at the 1959 symposium, i.e., that they are aggregates of F centers ($M = F_2$, $R = F_3$, $N = F_4$). M. Ueta, M. Hirai, and M. Ikezawa (Tohoku) presented optical evidence of M' , R_1' , and R_2' centers, formed by temporary trapping of electrons by the well-known "normal" M , R_1 , and R_2 centers.

The F_A center, a new color center with a $\langle 100 \rangle$ symmetry axis described by F. Lüty (Stuttgart) at the 1959 symposium, had since been shown by him and his co-workers and by Kojima, et al., to be an F center in which one of the cations bordering the vacancy is a foreign alkali ion, such as Na^+ or Li^+ in KCl. Photoconductivity and ESR studies of the F_A center were reported by H. Ohkura and K. Murase (Osaka), and an extensive investigation of the polarization properties and temperature dependence of the absorption and emission spectra of this center was described by Lüty and W. Gebhardt (Stuttgart).

The F_A -center studies of the latter investigators supplemented their studies of the temperature dependence of the spectral distribution of the F -center luminescence, which resulted in a determination of the vibrational frequency interacting with the excited state of the F center. Lüty and Gebhardt summarized the data on "normal F " and F_A centers by means of configuration-coordinate diagrams which have unusual features. In the ground state of both centers the interaction is with the cubically symmetrical breathing mode of oscillation of the ions bordering the vacancy; while, due to a noncubic lattice relaxation after the optical transition, the coupling in the excited state is with a vibrational mode having tetragonal symmetry. In the F_A center, the excited state is split into two components due to the mass defect of the "disturbing" foreign ion bordering the vacancy. An infrared emission of the KCl:Na F_A center, predicted on the basis of such c-c diagrams, was observed experimentally. These experimental results and the rather unorthodox configuration-coordinate treatment offer interesting ground for further theoretical work.

Additional stimulus to theoretical work was offered by Lüty's experiments on the higher excited states of the F center, a continuation of the work he first announced at the 1959 symposium. He showed that the K and L bands are shifted as a consequence of the $F \rightarrow F_A$ conversion, and that dichroism is observed in the K and L absorptions of the F_A center as well as in the F_A absorption itself, firmly establishing the interpretation of the K and L bands as absorptions which lead to transitions to higher excited states of the F center. The results were again summarized in terms of a configuration-coordinate analysis; this predicted a new F -center luminescence from the excited state which was observed at low temperature.

Further theoretical questions were raised by R. K. Swank and F. C. Brown's (U. of Illinois) report on measurements of the lifetime of F centers in the excited state, which was found to have the unexpectedly high

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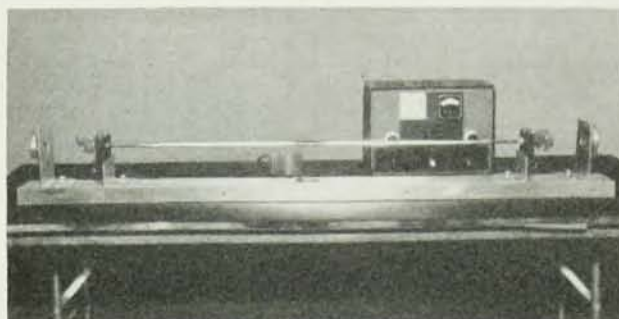


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value of about 10^{-6} second. A. Miehllich (Stuttgart) reported on the concentration dependence of efficiency of F -center luminescence which led to the conclusion that quenching interactions take place between F centers separated by as much as 13 lattice constants.

The use of electron spin resonance as a tool for studying color centers was discussed in about twelve papers. Topics included the observation of the resonance of impurity atoms, the search for the resonance of centers arising from aggregated F centers, the study of the relaxation mechanisms of the F center, and the study of the ESR absorption band of F centers which have been optically bleached. The work of Moran and Silsbee (Cornell), Noble (Armour Research Foundation), and Seidel (Stuttgart) pointed out the difficulties which remain in understanding the fundamental aspects of the relaxation of the F center. The change in the absorption line shape, and in the saturation behavior of the F -center ESR absorption band which occurs upon optical bleaching of the F center was interpreted by Schworer and Wolf (Stuttgart) as arising from a weak exchange interaction between F centers which are separated by a few lattice constants. Similar conclusions were drawn from studies of neutron-irradiated LiF by Bray and Kaplan (Brown). The electron spin resonance therefore, seems capable of providing valuable information concerning the distribution of color centers in a crystal.

Many papers were devoted to the study of impurity effects and impurity centers in alkali halides, with emphasis on the anionic impurities such as hydroxide, hydride, oxygen, carbonate, and sulfate. A particularly interesting contribution was the paramagnetic-resonance study by W. Känzig (ETH, Zurich, and GE Schenectady) of the alignment of the anisotropic O_2^- center by mechanical stress. This center consists of an O_2^- molecule-ion substituting for a halide ion, the internuclear axis of the center having six possible equilibrium orientations along the $\langle 110 \rangle$ axes of the alkali-halide crystal. Mechanical stress lifts the sixfold orientational degeneracy, producing population differences which correspond to an alignment of the centers. The kinetics of this process were studied over the temperature range of 1.5 to 33°K. It was found that the O_2^- molecule-ions do not freeze in, and that the reorientation rate is not given by the usual reaction-rate theory.

At the symposium banquet, an eloquent tribute was paid to Prof. Prziabram by Prof. Pick, who reviewed the contributions of the Vienna School to the study of color-center phenomena. At a postconference party, held at the Institut, the participants were treated to a high-spirited sketch, written and acted by the graduate students, lampooning the present status and future course of color-center research at an imaginary "World Color-Center Center". The excellence of the conference arrangements and the hospitality of the hosts were in the best tradition of the previous color-center conferences.