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Photochemical Conversion of Color Centers in Heated Crystals of Potassium Chloride

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The results of investigating the photochemical conversion of *F*-centers in KCl crystals at temperatures of 270-300° C, leading to the complete disappearance of absorption *F*-bands and their replacement by analogous symmetrical bell-shaped band (*X*-bands) displaced by 0.5 ev towards the long wavelength region, are described.

At lower temperatures (250-150° C), exposure to light similarly results in the complete disappearance of *F*-bands and their replacement by wider and lower symmetrical absorption bands somewhat displaced toward the long wavelength region.

The temperature dependence of absorption *X*-bands is characterized by increasing height, narrowing, and displacement of the bands towards shorter wavelengths, upon cooling. Preliminary measurements of the kinetics of the photochemical conversion process of *F*-centers are reported for different temperatures. A hypothesis connecting the observed thermophotochemical *F*-center conversions with the formation process of colloidal alkali metal is proposed. The possible mechanism of converting *F*-centers into F_2-centers is deduced.

1. STATEMENT OF THE PROBLEM AND THE METHOD OF MEASUREMENT

THE rapid growth of the various applications of electron flow in dielectric crystals and semiconductors has necessitated an experimental and theoretical investigation of localized electron concentrations near different lattice imperfections. The knowledge of the properties and the structure of such states is imperative, in particular, for the understanding of early stages of thermal and photochemical processes involved in coloring transparent solids.

For certain applications, it is also particularly important to understand the conversion of initial "atomic" color centers into colloidal aggregates containing millions of neutral metal atoms.

Recently it has been repeatedly admitted in the literature that silver halide is not useful in the detailed study of the photochemical process, despite its practical importance in such processes. Even at room temperatures, the significantly high mobility of the cations causes considerable difficulty in investigating the correspondingly rapid coagulation of silver following exposure to visible light. Moreover, the investigation of photochemical conversions by means of absorption spectra is further limited in the visible region by self-absorption by the lattice. Much more suitable for such investigations are monocrystals of alkali-halides This is due to their higher melting points, the correspondingly higher temperatures of other transitions depending on ionic mobility, their insensitiveness to visible light under normal conditions, and the transparency of pure compounds in a wide spectral range.

Taking into account these advantages and the observation first made by Kravtse[1] in 1928, and fully accepted today[2], viz., the analogy between photochemical processes in silver halides and alkali halides, it is natural to use alkali-halides in the role of "models" for silver halides in the solution of many problems.

For these "models", as distinct from silver halide*, the name *F*-center was adopted for the initial atomic centers of high-temperature colloidal coagulates.

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* Kirillov[3] has shown that for silver halide the absorption centers are intermediate between atomic and colloidal. However, the initial primitive absorption centers were not observed experimentally. The possibility of identifying with *F*-centers absorption bands observed by Meikliar[4] near the actual absorption edge of AgBr and AgCl crystals, irradiated by ultraviolet or heated, is open to discussion[5].

[1] S. I. Vavilov, Uspekhi. Fiz. Nauk 27, 106 (1945).

[2] P. V. Meinkliar, Uspekhi Nauch. Fotogr. 1, 149 (1951).

[3] E. A. Kirillov, Izv. Akad. Nauk SSSR, Ser. Fiz. 12, 533 (1948); Uspekhi. Nauch. Fotogr. 1, 183 (1951).

[4] P. V. Meikliar, Izv. Akad. Nauk SSSR, Ser. Fiz. 26, 129 (1952).

[5] O. F. Tomasevich, Thesis, Kiev State University, (1952).

Despite the apparent multi-stepped process of colloid formation, up to now it has been possible to obtain the final products of this process in alkali halide crystals only in the form of multi-atomic particles of alkali metal**.

Certain foreign investigators have even reached the conclusion*** that at temperatures allowing ionic mobility only "coarse" photochemical conversions take place, intimately associated with the permissability of ionic transitions. Finer photochemical reactions, determined by photo-transitions of electrons and also their local fixation (except *F*-centers), can only be accomplished at low temperatures.

It is not possible to agree with this conclusion because in the first stages of the photochemical coagulation process even the simplest conversions are essential, beginning with the action of individual photons, through their statistical distribution in the crystal lattice, to their absorption by the *F*-centers. However, until very recently, it has not been possible to determine what the nature of this initial light effect is and what local electronic conditions follow immediately after the photochemical annihilation or combination of *F*-centers, i.e., it was not possible to determine the intermediate production of atomic and colloidal centers, which, without any doubt, exist here similarly as in silver halide.

Wishing to advance the explanation of this question, we attempted to study changes in absorptivity of KCl crystals containing *F*-centers under the influence of light at elevated temperatures. Some of the results of our measurements have been described in a preliminary publication[7] In the present publication we describe in greater detail the applicable method and further investigations.

The absorption spectra of alkali halide crystals additionally colored were studied on specimens "frozen to room temperature after coloring at elevated temperatures. The temperature dependence of absorption was studied by heating and cooling these specimens to the desired temperature. This method is not without fault, however, since in cooling, no matter how quickly done, as well as in heating, it is possible that processes changing the distribution an properties of the color centers take place in the crystals. Such processes may be: the crystals becoming transparent, possible conversion of the centers, coagulation of colloids, etc. This shortcoming cannot be circumvented in the measurement of absorption by crystals colored in alkali-metal vapors.

The overwhelming majority of foreign investigations have been, and are presently being carried out, on crystals colored by exactly this process. Yet, an alkali halide crystal can be easily colored additively by diffusing the color from a sodium electrode into a warmed crystal[8]. In this method, the electrons enter the crystal voluntarily (electron diffusion) or under the coercion of an applied field. Taking advantage of this application, we developed a method[9] for obtaining colors of uniform intensity by forming them in a homogeneous electrical field with the aid of planar parallel electrodes. The method of coloring with a sodium electrode eliminates the need of a vacuum and if an applied electric field is used it is possible to make the crystal transparent repeatedly, and to color it.

The utilization of this method permitted us to measure the absorption spectra of the crystals, located directly in the oven, at various temperatures and degrees of coloration. The samples under investigation were potassium chloride monocrystals grown by the method of Kiropulius with every precaution being taken to attain maximum purity. A ray diagram of the actual experimental arrangement is schematically pictured in Fig. 1.

The samples were cleaved from a monocrystal to a size approximately 2.5 × 1.5 × 0.5 cm, carefully polished on two sides and placed between two sodium electrodes with the aid of a support *A*. This assembly was placed in a horizontal cylindrical oven, *B* supplied with transparent windows, *C*. The light from a rectangular 30 watt tungsten source, *D*, powered by a storage battery, passed through a condenser lens which focused the light on to the surface of the crystal plate *E*. The transmitted light passed

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** The explanation of low, longwave absorption bands obtained by Petroff[6] and other investigators in terms of absorption by aggregates of atomic centers resulting from light acting on the *F*-centers at low temperatures appears highly debatable.

***See the foreward written by R. W. Pohl and H. C. Pick to the investigation by Petroff[6].

[6] St. Petroff, Z. Physik 127, 443 (1950).

[7] A. A. Shatalov, Dokl. Akad. Nauk SSSR 92, 3 (1953).

[8] S. A. Artsybyshev, Trudy Phys. Inst. Akad. Nauk SSSR 1, 3 (1938).

[9] A. A. Shatalov, Trudy Phys. Facult. Kiev State University 6, 43 (1952).

through another lens which focused the light on an aperture, F, placed in front of a UM-2 glass monochromator. The intensity of the light passing through the monochromator was measured with a galvanometer and a photosensitive element (selenium, FES, FES-U), which was sensitive to the various spectral regions.

Since we were only interested in measuring the change of shape and position of the peaks and not the absolute value of the absorption coefficient μ, we did not have to measure the thickness d, of the the absorbing layer, and we selected the magnitude of $\ln \frac{I_0}{I} = \mu d$ as a measure of the absorption.

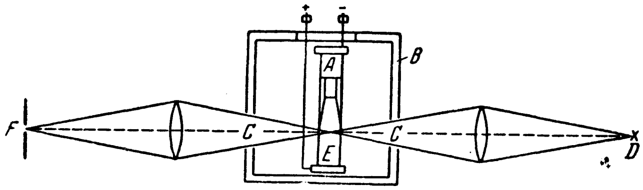

FIG. 1.

The intensity of the incident beam, I_0, was measured by passing the light through the crystal, made transparent by reversing the applied field. In this way, we could avoid all the errors arising from surface reflections, surface irregularities, etc., since the same conditions were used for measuring I and I_0.

The simplest effect of the intensity of the light on the crystal could be realized in the following way. The beam of light used for the measurement constituted a light probe formed by the focal spot on the crystal surface. Its intensity depended, therefore, on the conditions of focusing (area of spot) and on the variable intensity of the light source. Later, the effect of the light was also realized on large uniformly lighted areas.

2. EXPERIMENTAL RESULTS

As has been reported previously[7], the light absorbed in the range of an F-band does not lead to its destruction up to temperatures of ~ 300° C. However, upon slight further cooling, a distinct light sensitivity of the F-centers develops resulting in a conversion, during a few seconds following the beginning of the exposure, from a blue-violet atomic coloring of the crystal into a less intense (due to absorption near the boundary of the visible spectrum) blue having a greenish tinge.

As soon as the light source was turned on, a small "window" formed on the uniformly colored background due to the F-centers. This window had sharply outlines boundaries corresponding exactly to the shape of the light probe. Within the area of this window, the above-described color changes took place, corresponding to the formation of new color centers. The further path of the light beam passed only through the region of the new color, making possible the measurement of the absorption spectra of this region. The degree of complete "saturation" attained could be measured by observing the galvanometer indicator after rotating the monochromator to the position corresponding to the wavelength of the F-peak. Experiments with copper sulfate and yellow glass filters, serving to connect the long and short wavelength ends of the spectrum, permitted the determination of the photoactivity of the light absorbed in the region of the F-band.

By means of measurements at temperatures of 300-270° C, it was determined that the effect of exposure to light resulted in a replacement of the F-peaks in the long wavelength region by bell-shaped absorption bands centered approximately near 740 $m\mu$. In all other regards, the new absorption band, which we have called the X-band, does not differ significantly from the original F-band.

In Fig. 2, curve a represents the F-band observed at 270° C by a method wherein light pulses are used that are long enough to allow measurement (with a damped galvanometer) but not long enough to allow significant changes in the color centers. Curve *b* shows the change in the absorption of the crystal brought about by continuous exposure of the crystal until it had been "saturated." At the indicated temperatures the *X*-band is thermally unstable, disappearing in a short time interval, depending on the temperature, if the light source is removed. In this case, the crystal returns to its original color and the *F*-band is restored to its former intensity. The *X*-band can be frozen in only by rapidly quenching the crystal to room temperature. In this case, it is perfectly stable both in the dark and under visible light. The photochemical destruction and thermal reconstruction of the *F*-centers can be repeated many times.

Exposure to light at temperatures of 250, 200, and 150° C can also destroy the *F*-band completely. However, essential differences are observed. The optical destruction of the *F*-centers takes place at different rates, passing through a maximum (see below), and decreasing with decreasing temperature.

Moreover, upon termination of the exposure, the newly formed centers disappear more slowly as the temperature decreases until they reach thermal stability, which point is a function of the original *F*-center concentration. The observed thermophotochemical conversions are irreversible, and only by raising the crystal temperature to 270-300° C or higher can the original *F*-band be restored in a purely thermal way. Furthermore, the coloring of the crystal resulting from exposures at lower temperatures is different from the coloring caused by *X*-centers. This difference is characterized by the absorption curves (curves *c* and *d* in Fig. 2) obtained at 250 and 200° C. These curves are symmetrical but show a more rapid decline and displacement toward longer wavelengths as compared to the *X*-bands. The change is proportional to the drop in temperature.

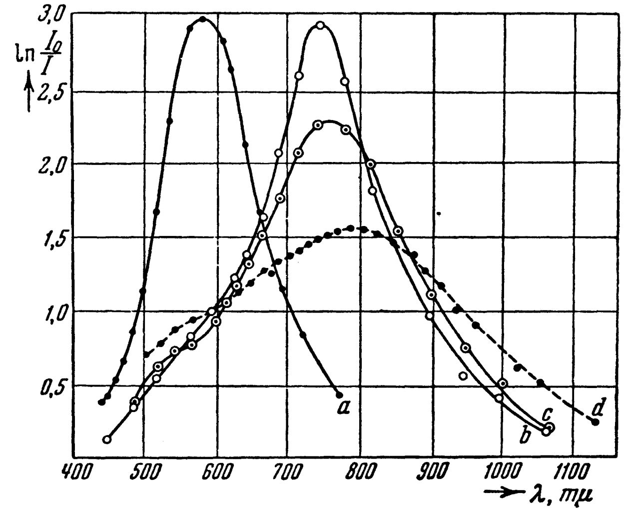

FIG. 2. *a*-*F*-centers, 270° C; *b*-*X*-centers, 270° C; *c*-colloids, 250° C; *d*-colloids, 200° C.

The effect of light below 150° C, when the observable ionic mobility is virtually absent, does not produce complete disappearance of the *F*-band and leads to a considerably slower production of photodisintegrated *F*-centers having absorption curves with many maxima. The investigation of these curves, begun recently by Petroff[6], and their relation to our higher temperature observations will require further study.

By means of additional measurements we have elucidated the nature of the temperature dependence of the new absorption band. It can be seen from the observations reported previously[7] that for any chosen light intensity, provided it is sufficiently great, there exists a limiting temperature above which it is not possible to observe a complete conversion of *F*-centers into *X*-centers. Below this temperature, the observation of thermal changes in the pure X-band is possible only during continuous exposures or else by cooling in darkness until the temperature reaches the range of thermal stability of X-centers. Otherwise, the electrons have an opportunity to return to the F-levels and the changes in the X-bands are not produced solely by temperature change. On the right side of Fig. 3* are shown X-bands measured on the same exposed crystal at 280, 200 and 20° C. Intermediate temperatures yield curves intermediate between those shown. The increasing height and narrowing width of the peak, observed with decreasing temperature, obeys well the constancy of the product of the maximum absorption coefficient times the halfwidth. As is well known, the relation $\mu\delta = \text{const}$ for F-bands has been experimentally proven by many authors, and is quantitatively deduced in Pekar's[10] theory. This product (also constant for the X-bands shown) numerically is almost identically equal to its value for the original F-band measured after additional coloring at 500° C. The temperature dependence of this curve is shown on the left side of Fig. 3 for comparison purposes. As can be seen, the displacement of the two bands is quite different. Instead of the usual pronounced shift in the F-band, the X-band shifts but slightly in the direction of shorter wavelengths upon decreasing the temperature.

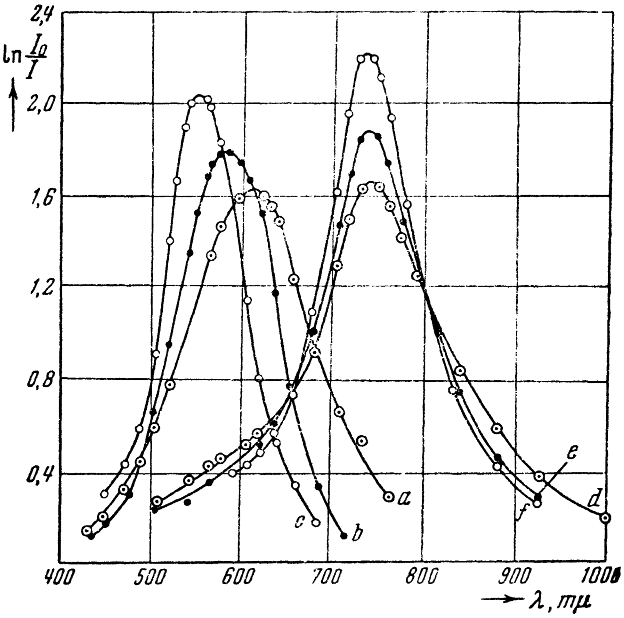

FIG. 3. a–F-centers, 500° C; b–F-centers, 280° C; c–F-centers, 20° C; d–X-centers, 280° C; e–X-centers, 200° C; f–X-centers, 20° C.

The kinetics of the photochemical conversion of F-centers into aggregations absorbing in the inner region of the spectrum can be best evaluated from the decrease in absorption in the F-band or by its increase in newly arising bands. After setting the monochromator on the maximum of an absorption band, the deflections of the galvanometer connected to the photoelement on which the light falls after passing through the crystal and the monochromator are measured. Recording these deflections at fixed time intervals, and assuming the magnitude of $\ln = \frac{I_{0\,\max}}{I_{\max}}$ as a measure of the

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* The measurements reported in Fig. 3 were carried out by L. M. Titomir.

[10] S. I. Pekar, *Investigation of the Electronic Theory of Crystals*, GITTL, 1951.

concentration*, one can obtain an approximate time dependence of the latter for disappearing and newly formed centers under different conditions.

The curves in Fig. 4 are examples of isotherms of time dependent *F*-center concentrations, obtained by us in this way. The functions at 280-270° C, corresponding to the conversion of *F*-centers into *X*-centers, have an exponential character as can be shown by the usual graphical analysis. As the temperature is lowered the curves become hyperbolic and then straighten out to become linear. This lack of congruency in the curves indicates a change in the nature of the *F*-center destruction mechanism with change in temperature. In addition, the curves show that the rate of conversion also depends on the temperature . It would have been easy to select an observational parameter to follow this dependence if the curves all had the same shape. For example, in the case of an exponential fall-off in the concentration, a useful parameter of process rate (radioactive disintegration) is the so-called disintegration constant (magnitude equal to the reciprocal half-life) which is a coefficient in the exponent and determinable from the slope of the line: logarithm of the concentration vs. time. In this case, as an approximate common characteristic of the observed function, the time τ of half-disintegration of *F*-centers, can be chosen, i.e,, the time, essentially different for different temperatures, during which the concentration of *F*-centers is decreased by one-half. The magnitude of the reciprocal of this time can then be used as an indication of the rate of the process.

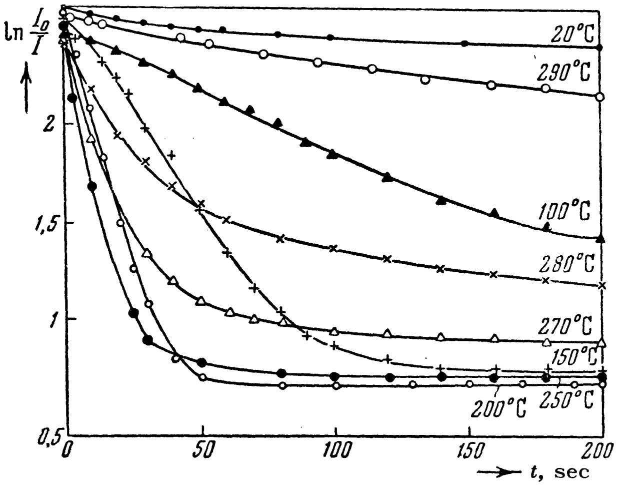

FIG. 4.

If we plot $1/\tau$ as the ordinate and the temperature as the abscissa, we obtain the curve shown in Fig. 5. It shows that the rate of photochemical conversion of *F*-centers, very small at low temperatures (apparently bounded by an insignificant ionic mobility), grows rapidly with increasing temperature reaching a maximum near 240° C. This part of the curve is reminiscent of temperature dependences (e.g., conductivity or diffusion) governed by the temperature increase in ionic mobility. This fact, as well as the temperatures at which the increased rates begin, convincingly testify that the thermophotochemical conversions of interest to us are connected with ionic rearrangements. After attaining a maximum, the rate curve falls rapidly. This appears to be a consequence of a sharp growth of a reverse thermal decomposition of new formation, beginning at certain temperatures.

We have measured the temperature dependence of reconstitution of *f*-bands after discontinued exposure, and also the appearance of *X*-bands and their thermal disintegration. These dependencies,

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* Since, at not overly large concentrations (in the absence of interactions between centers) the halfwidth of the absorption band is independent of the concentration, the latter can be assumed to be proportional to the absorption coefficient at the maximum, for independent centers and constant temperature.

along with quantitative analyses of the kinetics of photochemical conversions of F-centers into X-centers will be published in the near future.

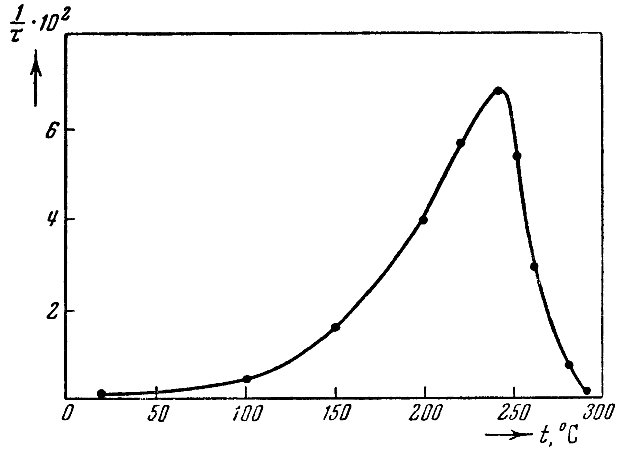

FIG. 5.

3. CONCLUSIONS

The experimental results at our disposal do not permit a complete elucidation of the mechanism of the conversion of F-centers into new color centers, nor the determination of the exact nature of the latter, However, the sequence of established facts already gives us reason for connecting the observed conversions with the colloidal coagulation of F-centers. This is especially evident for formations characterized by lower and broader curves shifted toward longer wavelengths (see Fig. 2), which can be attributed to absorption by ever increasing colloidal aggregates according to the calculation of Savostianova[11].

As a matter of fact, the color centers observed by us produce absorption bands shifted towards longer wavelengths as compared to the F-band and can be obtained as a result of affecting the color of the crystal by heat and light, i.e., the same factors that figure in the processes of colloidal coagulation, specifically at those temperatures at which this coagulation takes place in alkali-halide crystals.

As is well known, the rate of purely thermal colloidal coagulation is practically equal to zero for sufficiently high and sufficiently low temperatures. Consequently, in the process of cooling, it must pass through a maximum. This is apparently the result of the temperature dependence of the following processes: As the temperature lowers, the speed with which the atomic centers conglomerate increases with an initial formation of multiple centers and later of colloidal aggregates. It is believed that the outset of this process must be characterized by a certain saturation concentration of atomic centers in the crystal, which decreases upon cooling, similarly to the process taking place, for example in the precipitation of the solid phase from a saturated liquid solution. Moreover, the rate of the reverse process, i.e., the dissociation of the colloid into atomic centers, is also decreased with lowering temperature. At certain specific temperatures, however, an equilibrium between these two processes exists. If, in a crystal being cooled, after such an equilibrium condition has been reached, the intensity of the first process were to predominate again, the rate of colloidal coagulation could grow without limit. However, this growth is limited by the appearance of a third factor, viz., a rapid decline and, finally, a complete stoppage of the ionic mobility. The influence of this factor sharply decreases the rate of colloid formation, forcing it again to drop from the maximum.

Upon cooling, the state of the crystal immediately preceding the dynamical equilibrium of

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[11] M. V. Savostianova, Izv. Phys. Mat. Inst. Akad. Nauk SSSR 3, 169 (1930); Z. Physik 64, 262 (1930).

the processes of coagulation and dissociation, according to our observations, appears at temperatures at which the photochemical formation of X-bands is possible.

From the results of the present investigation, it is possible to reach the conclusion that two processes, analogous to those described above, occur in potassium chloride also. As an additional condition to the process of purely thermal coagulation, there appears here the role of exposure to light. The latter leads to an optical destruction of F-centers at temperatures too high for thermal coagulation. The thermal decomposition of the new formations combined with the reconstitution of F-centers makes up the second process. In this way, exposure to light is capable of initiating photochemical coalescence of atomic centers somewhat earlier than would be the case thermally, and at the same time displaces the initiation of the coagulation process toward higher temperatures, preceding those at which saturation concentrations occur. This latter condition predetermines the thermal instability of X-centers.

The presence of a maximum in the temperature dependence of the ratio in the observed optical process, has been shown by us in Fig. 5. Being bounded on the top by a rapidly growing thermal instability, and at the bottom by a fall-off in ionic mobility, the thermophotochemical process of conversion of F-centers can take place only in a narrow temperature interval. This further shows its similarity to the process of colloid formation.

As far as the nature of X-centers is concerned, we can make a fairly reliable choice between a representation of X-centers as more or less sizable colloidal aggregates containing large numbers of alkali metal* and an assumption that they are simple nuclei, possibly associated with the initiation of colloidal coagulation, being either new mono-atomic centers or small groups of atoms resulting from the coalescence of F-centers. The sequence of arguments[7] convincingly testifies in favor of the second postulate.

A more concretely plausible possibility appears to be a model identifying X-centers with F_2-centers. Such a model agrees well with the observational facts and theoretical considerations of Deigen[13] (the position of an absorption curve's maximum, its intensity, halfwidth, binding energy, etc.). On its basis, the mechanism of photochemical reaction observed by us can be explained more simply as a phototransition of an electron from an absorbing F-center, with simultaneous formation of an F'-center and a halogen vacancy, followed by rapid recombination of the two into a double center according to the scheme: $2F \to F_2$. As is well known[14], F'-centers are extremely unstable at observational temperatures and would succeed in disintegrating up to the moment at which they are somewhat stabilized by combination with halogen vacancies, if the latter did not occur with sufficient rapidity, caused (aside from significant coulomb fields of opposite charge), by their sufficient mobility.

From this, the role of the presence of intense ionic mobility becomes clear, i.e., the sufficiency of high temperature to make possible X-center formation. The same can be said about the reverse process of rapid destruction of X-bands after terminating the exposure. This can be explained simply by thermal dissociation of double centers made unstable by the presence of ionic mobility. The latter is confirmed by the stability of X-centers following a rapid quenching to room temperature.

The proposed unstable formation, obtained by stabilizing an F'-center by combination with a halogen vacancy, appears to be a realization under rigid conditions of an earlier, experimentally unobserved local state of the electron in the crystal lattice. A more certain determination of its properties can be made only following continued investigation.

Translated by L. V. Azaroff
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* This apparently unlikely possibility must be mentioned, since Scott and Smith[12] who obtained a narrow long-wavelength absorption band in a KCl crystal by purely thermal means at very high initial concentrations, attributed this to a colloidal metal distribution and called it colloidal.

[12] A. B. Scott and W. A. Smith, Phys. Rev. 83, 982 (1951).

[13] M. F. Deigen, J. Exper. Theoret. Phys. USSR **21**, 992 (1951); **24**, 631 (1953).

[14] H. Pick, Ann. d. Physik **31**, 363 (1938).