Materials Science Center Report No. 1029, 1969 (unpublished).
[35]G. V. Chester (private communication).
[36]A. Lakatos and H. S. Sack, Solid State Commun. 4, 315 (1966).
[37]P. Clayman, I. G. Nolt, and A. J. Sievers, Solid State Commun. 7, 7 (1969).
[38]H. F. Macdonald, M. V. Klein, and T. P. Martin, Phys. Rev. 177, 1292 (1969).
[39]W. D. Wilson, R. D. Hatcher, G. J. Dienes, and R. Smoluchowski, Phys. Rev. 161, 888 (1967).
[40]A. F. Devonshire, Proc. Roy. Soc. (London) A153, 601 (1936).
[41]E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955), Chap. 7.
[42]T. L. Estle, B. Dischler, and R. W. Timme, Bull. Am. Phys. Soc. 14, 346 (1969).
[43]M. Gomez, Ph. D. thesis, Cornell University, Materials Science Center Report No. 910, 1968 (unpublished).
[44]G. Benedek (unpublished).
[45]W. Dreybrodt and K. Fussgaenger, Phys. Status Solidi 18, 133 (1966).
[46]Dr. B. Wedding and Professor M. V. Klein kindly gave us several OH^-- and OD^--doped NaCl crystals which had been analyzed for OH^- concentration.
[47]R. Rosenbaum and M. V. Klein, Phys. Rev. (to be published).
[48]W. R. Fenner, Ph. D. thesis, University of Illinois, 1969 (unpublished).
[49]Dr. D. R. Bosomworth supplied the NaCl sample doped with 1500-ppm OH^-.
[50]Harshaw Chemical Company, Cleveland, Ohio.
[51]Dr. R. K. Skogerboe and the Materials Science Center Analytical Facility analyzed the samples for impurity concentration using flame-emission techniques.
[52]P. Sauer, Z. Physik 194, 360 (1966).
[53]C. K. Chau, M. V. Klein, and B. Wedding, Phys. Rev. Letters 17, 521 (1966).
[54]H. B. Shore, Phys. Rev. Letters 17, 1142 (1966).
[55]M. E. Baur and W. R. Salzman, Phys. Rev. 151, 710 (1966).
[56]R. S. Scott and W. H. Flygare, Phys. Rev. 182, 445 (1969).
[57]A. M. Stoneham, Proc. Roy. Soc. (London) 89, 909 (1966).

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Formation of F_2^+ Centers in KI†

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When undoped KI is x rayed at 130 °K and then irradiated with F light at 240 or 270 °K, the M and R centers are formed. Subsequent irradiation at 78 °K with M_L light results in the formation of an optical-absorption band at 1650 nm at the expense of the M band. Studies suggest that it is associated with F_2^+ centers (formerly called M^+), which are formed at 78 °K by (i) $V+F_2+(M_L \text{ light}) \rightarrow V^-+F_2^+$ (where M_L light represents light absorbed by the M_L bands) and destroyed by x rays at 78 °K, by (ii) $V^-+F_2^++(\text{x rays}) \rightarrow V+F_2$ [where V^- is an electron center containing a halogen (V) center core]. F_2^+ centers may also be destroyed at 78 °K by F light, by (iii) $V^-+F_2^++F+h\nu_F \rightarrow V^-+F_2+\alpha$. Studies show that the F_2^+ center is not formed optically as a result of V_K excitation, but only by direct ionization. The formation of F_2^+ centers by M_L-light irradiation in x-rayed colored crystals seems to depend on the existence of V centers which act as special electron traps.

I. INTRODUCTION

It is well known that F-band irradiation of alkali halides near room temperature results in the formation of M, R, and N bands. The M, R, and N bands are called F-aggregate centers and are formed on the longer wavelength side of the F band.[1] The various F-aggregate centers so far mentioned are electrically neutral clusters of anion vacancies and trapped electrons. If additional electrons are trapped (by F-aggregate centers), one would have F_2', F_3', and F_4' centers (where the prime denotes an additional electron) having an effective negative charge.[2] On the other hand, if electrons are removed from F-aggregate centers, one would have F_2^+, F_3^+, and F_4^+ centers having effective positive charge. With either positively or negatively charged F-aggregate centers, one must have complementary centers of opposite charge in the crystal. Recently, a number of studies have been reported on absorption bands associated with ionized F-aggregate centers (F_2^+ and F_3^+) in several alkali halides.[3-8]

The present work deals specifically with the observations of F_2^+ centers in KI and with the mechanism of formation and destruction of F_2^+ centers.

The mechanism of formation and destruction of F_3^+ centers in KI has been previously reported.[9]

II. EXPERIMENTAL PROCEDURE

The specimens of KI were cleaved from single large crystals obtained from the Harshaw Chemical Co. The optical-absorption measurements were made using a Cary Model 14R spectrophotometer in a previously described[10] optical cell.

The x rays were generated from a General Electric x-ray machine, No. OX-140 tube with a tungsten anode, operated at 125-kV peak, 4.5 mA, and 120 cps.

Undoped KI was x irradiated at 130°K, where the efficiency of coloration is maximum.[11]

In order to produce F-aggregate centers, the colored crystals containing F and V centers were optically irradiated in the F band with F light at several higher temperatures (240 or 270 °K). The F light was obtained by using a projection tungsten lamp and an interference 666-nm filter from Optics Technology, Inc. The so-called M_L light[12] was obtained by using a xenon-mercury high-pressure lamp Hanovia 510-B type and an interference filter (peak transmission at 405 nm, band pass 20 nm). The F-aggregate light was obtained by using a projection tungsten lamp and a Corning No. 7-56 glass filter.

III. RESULTS

A. Optical Formation F_2^+ Centers by M_L Light Irradiation at 78 °K

The crystal was first pretreated to contain mostly F_2 and some F_3 centers as shown in Curve 1 of Fig. 1. The crystal was then bleached with F-aggregate light at 78 °K (Curve 2, Fig. 1) to form

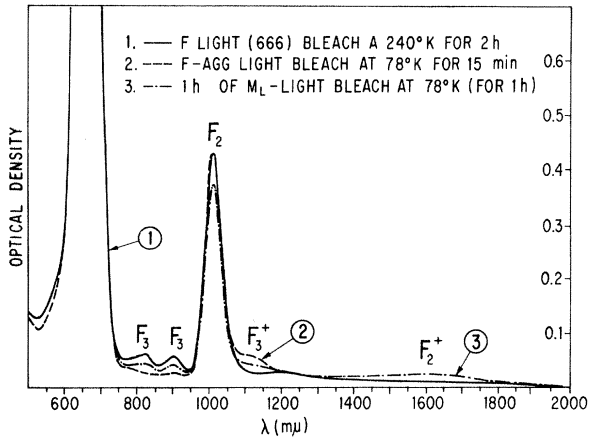

FIG. 1. Formation of F-aggregate centers at 240 °K in undoped KI by F light irradiation (Curve 1). Transformation of $F_3 \rightarrow F_3^+$ at 78 °K by F' light irradiation (Curve 2). Transformation $F_2 \rightarrow F_2^+$ at 78 °K by M_L light irradiation (Curve 3).

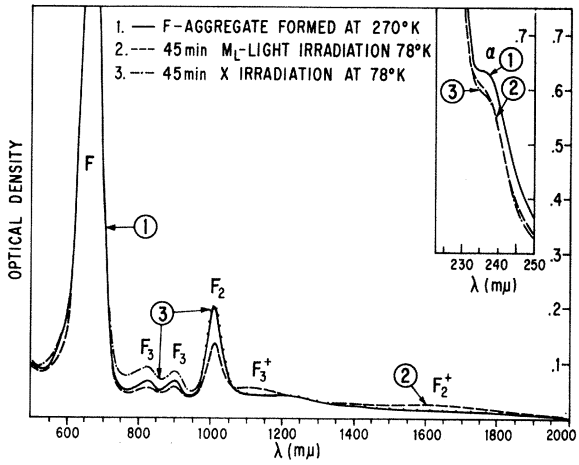

FIG. 2. Formation of F-aggregate centers at 270 °K in undoped KI by F light irradiation (Curve 1). Transformation of $F_2 \rightarrow F_2^+$ and $F_3 \rightarrow F_3^+$ at 78 °K by M_L light irradiation (Curve 2). Conversion of $F_2^+ \rightarrow F_2$ and $F_3^+ \rightarrow F_3$ at 78 °K by x irradiation (Curve 3).

F_3^+ centers,[9] but no F_2^+ centers were formed. Using the broad-banded infrared radiation to produce F_3^+ centers (1125-nm band) serves the additional purpose of bleaching any photoionizable centers such as F_2' and F_3' which might conceivably[2] be formed as a result of electron trapping by the F-aggregate centers. The same results were obtained by using R_2 light rather than F-aggregate light.[9] (The R_2 light was obtained by using a projection tungsten lamp and an infrared interference 900-nm filter with a band pass of 25 nm from Optics Technology, Inc.)

Curve 3 of Fig. 1 shows the results of the formation of a new broad optical-absorption band at 1650 nm at the expense of the F_2 band by irradiating the crystal with M_L light for one hour at 78 °K. Note that some F_3^+ centers were reconverted to F_3 centers as a result of M_L light irradiation.

In a new set of experiments (using a fresh crystal) the relative concentration of F-aggregate centers formation (Curve 1 of Fig. 2) were purposely made smaller than the concentration of the previous set of experiments (Curve 1 of Fig. 2). In this second set of experiments, the crystal containing F-aggregate centers (Curve 1 of Fig. 2) was subsequently irradiated for 45 min with M_L light at 78 °K instead of irradiating it with F-aggregate light. The results are shown in Curve 2 of Fig. 2. The new optical-absorption band at 1650 nm was formed at the expense of the F_2 band. Note that in this set of experiments, 50% of the F_2 centers were ionized. Note also that F_3 centers were ionized with this so-called M_L light.[12] From these results it is reasonable to assume that there

are R_L bands associated with F_3 centers and may correspond to the electronic transition from the ground state of the F_3 centers to its excited states in the conduction band as in the case of F_2 centers.[12]

B. Destruction of F_2^+ Centers

At 78 °K there is no ionic mobility; thus if the 1650-nm band is truly due to an F_2^+ center, the retrapping of an electron at the F_2^+ center should result in the reformation of F_2 centers. By bleaching the F centers with F light at 78 °K, we should be able to recover the F_2 centers. Figure 3 shows that when the crystal is irradiated with F light at 78 °K, the 1650-nm band disappears, and at the same time the F_2 band arises. These results constitute conclusive proof that the new center which gives rise to the 1650-nm band must be an F_2^+ center. The fact that the F_3 bands arise also is not accomplished at the expense of the new 1650-nm band.[9] Note that the Curve 1 of Fig. 3 is the same optical-absorption spectrum as that shown by Curve 3 of Fig. 1.

Curve 3 of Fig. 2 shows the x-ray-induced destruction of the F_2^+ centers at the expense of the F_2 centers. At this irradiation temperature (78 °K) no new F centers are produced.[11] No changes occurred in the F band (not shown here) as a result of the x irradiation at 78 °K, nor did any change occur in the α band (see insert Curve 3 of Fig. 2). From Fig. 2 it appears that the x rays transfer the electron from some unknown electron trap back to the F_2^+ center. At this temperature (78 °K) the major effect of x radiation is the generation of recombination luminescence. It is possible that the luminescence plays a role in the electron transfer. This idea is substantiated by the experiments described above, where the F_2^+ center is destroyed with F light rather than with x rays.

IV. DISCUSSION

A. Necessity for Electron Trap

The above data clearly demonstrate the identity, formation, and destruction of F_2^+ centers. The interconvertibility of F_2 and F_2^+ centers without loss logically requires the presence of an electron trap. The electron trap is a halogen (V) center core.[9] When the halogen (V) center core traps an electron from an ionized F_2 center, it becomes an excess electron center and is called here a ψ center.

B. Mechanism of Formation and Destruction of F_2^+

From the foregoing data and considerations, one arrives at the mechanisms presented below. The rate of optically ionizing F_2 centers by M_L light irradiation at 78 °K seems to depend on (i) the ability to optically eject an electron from the F_2 center, and (ii) the ability of halogen (V) centers to trap electrons.[13,14]

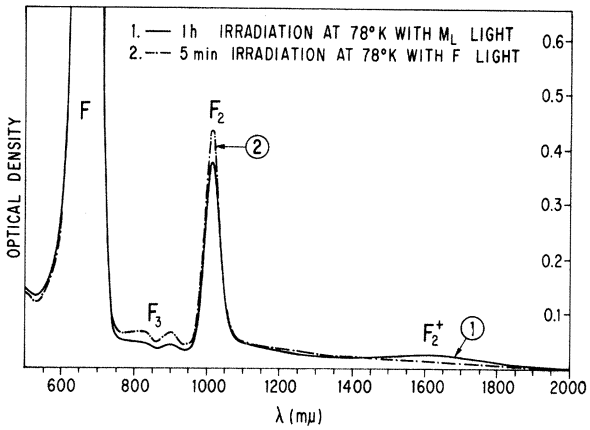

FIG. 3. Same optical-absorption spectrum as that shown in Curve 3 of Fig. 1 (Curve 1). Conversion of $F_2^+ \rightarrow F_2$ and $F_3^+ \rightarrow F_3$ at 78 °K by F light irradiation (Curve 2).

From the foregoing data and considerations, which are supported by observation, one arrives at the mechanisms presented below.

Case 1. The following are optical formation at 78 °K (using M_L light):

$$F_2 + M_L \text{ light} \rightarrow F_2^+ + e, \tag{1}$$

$$V + e \rightarrow \psi, \tag{2}$$

$$F_2^+ + \psi. \tag{3}$$

For Eq. (3) note Figs. 1 and 2.

Case 2. The following are optical destruction at 78 °K (using F light):

$$F + (F \text{ light}) \rightarrow \alpha + e, \tag{4}$$

$$F_2^+ + e \rightarrow F_2, \tag{5}$$

$$F_2 + \alpha. \tag{6}$$

For Eq. (6) note Curve 2 of Fig. 3.

Case 3. The following are x-ray destruction at 78 °K:

$$\psi + \text{x rays} \rightarrow V + e, \tag{7}$$

$$F_2^+ + e \rightarrow F_2, \tag{8}$$

$$F_2 + V. \tag{9}$$

For Eq. (9) note Curve 3 of Fig. 2.

V. CONCLUDING REMARKS

In this work, evidence was presented which strongly leads to the conclusion that the 1650-nm optical-absorption band in KI arises from transi-

tions of F_2^+ centers.

F_2 centers become ionizable, and their optical-absorption band is measurable when the electron ejected from an F_2 center becomes permanently trapped. The electron trap is a halogen (V) center core which forms an excess electron center called here the ψ center.

F_3 centers were also ionized by the so-called M_L light.[12] It is reasonable, therefore, to assume that there are R_L bands associated with F_3 centers just as there are M_L bands associated with F_2 centers.[12]

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[1]J. H. Schulman and W. D. Compton, *Color Centers in Solids* (MacMillan, New York, 1962).

[2]M. Hirai, M. Ikezawa, and M. Veta, J. Phys. Soc. Japan 17, 1474 (1962).

[3]I. Schneider and H. Rabin, Phys. Rev. 140, A1983 (1965).

[4]Y. Farge, G. Toulouse, and M. Lambert, Compt. Rend. 262B, 1012 (1962).

[5]L. F. Stiles and D. B. Fitchen, Phys. Rev. Letters 17, 689 (1966).

[6]J. Nahum and D. A. Wiegand, Phys. Rev. 154, 817 (1967).

[7]J. Nahum, Phys. Rev. 158, 814 (1967).

[8]J. Nahum, Phys. Rev. 174, 1000 (1968).

[9]A. Kouvalis and H. N. Hersh, Phys. Rev. 188, 1439 (1969).

[10]H. N. Hersh, Phys. Rev. 105, 1158 (1957).

[11]J. D. Konitzer and H. N. Hersh, Phys. Chem. Solids 27, 771 (1966).

[12]M. Hirai and K. Hashizume, in Proceedings of International Symposium on Color Centers in Alkali Halides, Rome, Italy, Abstract No. 84, 1968 (unpublished).

[13]A. Kouvalis, Bull. Am. Phys. Soc. 13, 73 (1968).

[14]A. Kouvalis and H. N. Hersh, Bull. Am. Phys. Soc. 13, 419 (1968).

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Mechanical Stability of Crystal Lattices with Two-Body Interactions

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The stability criteria developed by Max Born are applied to investigate the mechanical stability of body-centered-cubic (bcc) and face-centered-cubic (fcc) Morse-function crystal lattices { i.e., lattices in which the atoms interact via the morse interatomic potential energy function $\varphi(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}]$}. It is shown that the conditions for stability can be expressed uniquely as a function of αa, where a is the lattice parameter of the crystal. The fcc lattice is stable for all values of αa, while the bcc lattice is stable only for values of αa which are less than 4.8. The possibility of using Morse-function lattices to represent cubic crystals with particular values of elastic moduli C_{11} and C_{12} is investigated. The Morse function can serve quite well for this type of representation for fcc crystals. For bcc crystals, however, the ratio C_{11}/C_{12} does not exceed about 1.36; thus the representation is inherently fairly poor.

INTRODUCTION

Max Born[1] investigated the conditions under which a crystal lattice will be thermodynamically stable. Necessary conditions for the thermodynamic stability of a crystal lattice are that the crystal be mechanically stable with respect to arbitrary (small) homogeneous deformations. Born[1] derived mathematical expressions for these stability requirements (referred to as the Born stability criteria) for cubic lattices of the Bravais type on the assumption of central forces of a very general type.

In the present paper, the stability of cubic crystal lattices, in which the atoms interact via the two-body Morse[2] interatomic potential function, is investigated in terms of the Born criteria. This study was prompted by the fact that empirical two-body interatomic potential functions such as the Morse or the inverse power functions are often used for representing interatomic interactions in investigations of a wide variety of phenomena. For example, these functions have been applied to studies[3] of elastic moduli of metals[4,5] and alloys,[6] lattice distortion at surfaces,[7,8] shock wave pro-