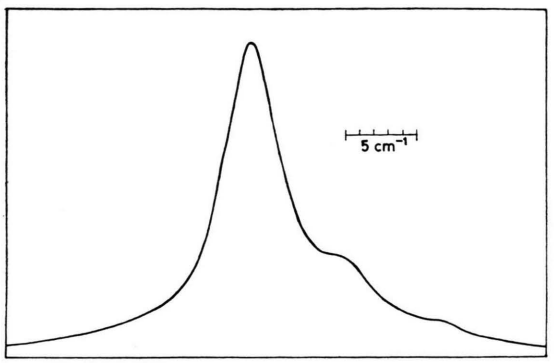

Abb. 3. Profil der 525 cm^{-1}-Bande bei hoher Auflösung.

Die hier geschilderten Experimente zeigen also im wesentlichen, daß die in reinem Methyljodid gemessene Bandenbreite der C–J-Schwingung Beiträge enthält, die auf die Einwirkung durch Nachbarmoleküle erzeugter lokaler Felder zurückzuführen sind, die hier ca. 4 cm^{-1} ausmachen. Nach einem groben Bild, das Polarisationseffekte vernachlässigt, wirken äußere Felder je nach Richtung verstärkend oder abschwächend auf polare Bindungen und beeinflussen somit über die Kraftkonstante die Schwingungsfrequenz. Der hier beschriebene Breiteneinfluß sollte deshalb auch bei IR-Messungen wirksam werden. Messungen der Konzentrationsabhängigkeit der IR-Bandenbreite haben das bestätigt. Die absolute Bandenbreite ist auf Grund der Rotationseinflüsse allerdings größer und entspricht damit der depolarisierten Komponente der Raman-Bande. Jedoch erscheint es nach dem hier geschilderten nicht zulässig, das summarische Profil einer solchen Bande der Berechnung einer Zeitkorrelationsfunktion der Rotation zugrunde zu legen. Durch geeignete Versuchsbedingungen sollten vorher andere Bandenbreiteneinflüsse eliminiert werden. Zeitkorrelationsfunktionen dieser Art wurden von Favelukes u. a.[7] für die Rotation um die Figurenachse aus der CH_3J-884 cm^{-1}-IR-Bande und für die Rotation um eine rechtwinklig hierzu stehende Achse aus dem IR-Profil der hier näher untersuchten C–J-Schwingung ermittelt. Nach Berücksichtigung des Bandenbreiteneinflusses nach c ergibt sich eine geringere Zerfallsgeschwindigkeit der Korrelationsfunktion.

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[7] C. E. Favelukes, A. A. Clifford u. B. Crawford jr., J. Phys. Chem. **72**, 962 [1968].

On the Nature of the N_1 Center in KCl

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Evidence is presented to show that the N_1 absorption band in additively colored KCl is identical with the R^+ band of Schneider and Rabin. Formation of this center gives an explanation for the low thermal stability of R centers. Thermal stability and mechanisms of formation and destruction of such ionized centers are discussed. Equivalent centers are postulated in other alkali halides. In KBr the reported positions of N_1 and R^+ bands are almost identical.

M and R centers have been shown by kinetic [1], thermodynamic [2] and electron spin resonance studies [3, 4] to be aggregates of two and three F centers respectively, but the nature of the N centers is still unknown although from analogy they might be expected to be complexes of four F centers as proposed by Pick [5]. Measurements of the relative intensities [6–8] and kinetics of formation [7, 9] and destruction [7] indicate that the N_1 band at about 960 nm [7, 9] and the N_2 band at 1028 nm [7] (1080 nm according to [9]) belong to different centers. According to kinetic studies [1] the N_2 center indeed contains four F centers while N_1 consists of only two. The R^+ center, that is a complex of two F centers and a negative ion vacancy, also has an absorption band at 960 nm [10] and it is the purpose of this paper to present evidence showing that N_1 and R^+ centers are, in all likelihood, identical. Such ionized F aggregate centers can be formed by redistribution of thermally liberated electrons leading to an equilibrium * between neutral and ionized centers:

$$\frac{n_\ominus}{n_F} = a(T)\,\frac{n_{M^+}}{n_M} = = b(T)\,\frac{n_{R^+}}{n_R} = \ldots \qquad (1)$$

[1] S. Schnatterly and W. D. Compton, Phys. Rev. **135**, A 227 [1964].
[2] J. D. Zahrt, A. B. Scott, and E. H. Coker, J. Chem. Phys. **46**, 791 [1967].
[3] H. Seidel, Phys. Letters **7**, 27 [1966].
[4] D. C. Krupka and R. H. Silsbee, Phys. Rev. Letters **12**, 193 [1964].
[5] H. Pick, Z. Physik **159**, 69 [1960].
[6] R. Hermann, M. C. Wallis, and R. F. Wallis, Phys. Rev. **103**, 87 [1956].
[7] S. Hattori, J. Phys. Soc. Japan **17**, 1454 [1962].
[8] W. E. Bron, Phys. Rev. **125**, 509 [1962].
[9] A. Halperin, A. A. Braner, M. Schlesinger, and N. Kristianpoller, Proc. Intern. Conf. Semicond. Phys., Prague **1960**, Czech. Acad. Sci., p. 724, Prague 1961.
[10] I. Schneider and H. Rabin, Phys. Rev. Letters **13**, 690 [1964].

* The term equilibrium means equilibrium distribution of electron with given distribution of anion vacancies, but not equilibrium distribution of anion vacancies in the crystal. This electron distribution is disturbed by generation of just one kind of ionized center, e. g. F^+ centers by F light illumination.

with $\ominus = \alpha = F^+$ being an isolated negative ion vacancy. The equilibrium constant $b(T)$ can be expected to have a smaller value than $a(T)$ (and presumably smaller than 1) due to the odd number of electrons in an R and even number in an R^+ center resulting in a high concentration of R^+ relative to all other ionized centers. This mechanism also gives an explanation for the thermal destruction of R centers at or slightly above room temperature not requiring migration of vacancies or vacancy pairs. It postulates growth of the N_1 band during thermal destruction of R centers and a small fraction of R centers pertaining up to temperatures high enough to permit dissociation of aggregates via migration of negative ion vacancies. Both effects have indeed been observed [7, 9], but the absorption remaining in the R_1 and R_2 band locations has been attributed to higher excited states of the N centers [7]. Heating experiments on bleached crystals should reveal a small temperature range of rapid decrease of aggregate centers to a lower concentration followed at higher temperatures by complete destruction of aggregates due to migration of negative ion vacancies. The temperature range of rapid destruction corresponds to equilibrium ratios $K_R = n_{R^+}/n_R$, $K_M = n_{M^+}/n_M$, ... close to one and is characteristic of the particular center, being lowest for the R center. These effects can be seen on the figure given by HALPERIN et al. [9, **].

HIRAI et al. [11] observed conversion of the N_1 band into R bands with F illumination at -110 °C, too low a temperature for vacancy migration. This experiment can be interpreted in terms of a redistribution of electrons according to the equation

$$F + R^+ \xrightarrow{h\nu_F} F^+ + R \qquad (2)$$

and is additional strong evidence for the R^+ model of the N_1 center.

The sum of all ionized centers in a crystal containing F and F aggregate centers should be equal to the number of isolated negative ion vacancies present before bleaching. This number is very small since the highly mobile cation vacancies readily combine with free negative ion vacancies to form vacancy pairs as long as their numbers are equal. Therefore ionized aggregate centers should be observable only in crystals containing more negative than positive ion vacancies due to the presence of divalent anions like O^{--} and S^{--}. O^{--} is a common impurity in additively colored crystals since OH^- group originally present are converted to O^{--} during additive colaration [12] giving rise to absorption bands in the UV at 430 and 283 nm [13]. A band near 1400 nm has been repeatedly observed in such crystals [12, 14–16]. It seems to be identical with the M^+ band of SCHNEIDER and RABIN [10]. Like the M band it reaches its maximum during early stages of bleaching [12].

In crystals free of divalent anion impurities (or with equal or higher numbers of divalent cation impurities) the ionized aggregate centers can be formed as unstable intermediates by thermal or optical ionization of aggregates. They can be converted back to aggregate centers by capturing an electron or they can combine with a cation vacancy thus forming a complex consisting of F centers and a vacancy pair. Again an equilibrium must exist between free vacancy pairs (symbolized by $\oplus\ominus$), F centers and aggregates and complexes of F centers with vacancy pairs:

$$\frac{n_{\oplus\ominus}}{n_F} = a'(T)\,\frac{n_{F\oplus\ominus}}{n_M} = b'(T)\,\frac{n_{M\oplus\ominus}}{n_R} = \ldots . \qquad (3)$$

The same arguments apply for the relative magnitude of $b'(T)$ as for $b(T)$ in Eq. (1). Evidence for such F center vacancy pair complexes has indeed been found [12]. The N_1 band on the other hand seems to occur only in crystals originally containing a considerable concentration of OH^- groups (like the extensively used Harshaw material) because no attempts were made to prevent hydrolysis during melt growth of the crystals.

Equivalent centers should occur in other alkali halides as well, but considerably less experimental work has been done on them. In KBr the positions of N_1 and R^+ bands have been reported at 1070 and 1020 nm respectively [10]. The difference is not larger than the uncertainty in the N_2 band location in KCl [1, 7] and additional experiments must reveal whether this difference is real.

I wish to thank Dr. ALLEN B. SCOTT for introducing me into this field of research and for valuable discussions on the subject.

** Reproduced in W. D. COMPTON and H. RABIN, Solid State Physics, Vol. 16, p. 190, New York, London 1964.

[11] M. HIRAI, M. IKEZAWA, and M. UETA, J. Phys. Soc. Japan **17**, 1483 [1962].

[12] G. LEHMANN and A. B. SCOTT (to be published).

[13] F. FISCHER, H. GRÜNDIG, and R. HILSCH, Z. Physik **189**, 79 [1966].

[14] F. OKAMOTO, Phys. Rev. **124**, 1090 [1961].

[15] H. RABIN, Phys. Rev. **129**, 129 [1963].

[16] F. FISCHER and G. GÜMMER, Z. Physik **189**, 97 [1966].