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Color Centers in Mixed Crystals of Alkali Halides*

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Single crystals of KCl, RbCl, KBr and mixed crystals of KCl-RbCl, KCl-KBr, and RbCl-KBr of various compositions have been colored by 3-MeV electrons with doses 10^4 to 10^6 rads at 20°, −80°, and −190°C. The influence of radiation dose, coloration temperature, and composition of mixed crystals on spectral position, half-width, and intensity of the V_1, K, F, F', and M bands has been studied. At room temperature K, F, and M bands were produced, and at highest coloration N bands; only F and K bands appear at −80°C. At −190°C coloration the V_1, K, F, and F' bands appeared. In mixed crystals the spectral position of all absorption bands deviates from the Mollwo relation ($\nu d^n=\text{const}$). The deviation in V_1, K, F, and M is toward lower, and in F' toward higher energy. The half-width of all bands in mixed crystals is greater than in pure components except that of V_1 in the KCl-RbCl system, where it is smaller. The intensity of coloration in KCl-RbCl decreases with composition and reaches a minimum at molar ratio 1:1. In KCl-KBr and RbCl-KBr the intensity curves exhibit a relative maximum and a relative minimum. The behavior of the observed color-center bands is correlated to crystal structure and to the configuration of color centers.

INTRODUCTION

INVESTIGATION of color centers in mixed crystals has been very limited up to now. Gnaedinger[1] studied the F bands in mixed crystals of several alkali halides grown in air and colored with x rays (50 kV, 20 mA) at room temperature. He obtained three main results: deviation of the F-band shift from the Mollwo relation[2] toward lower energies, broadening of the half-width, and lower coloration of mixed crystals. The same results have been obtained by Miessner,[3] who studied the KCl-RbCl and KCl-KBr systems. A study of the V_1 band was done by Miessner and Pick,[4] who found an S-shaped shift of spectral position with composition in KCl-KBr, while in KCl-RbCl the shift was approximately linear.

The broadening of the F band has been explained by assuming the superposition of seven elementary bands corresponding to seven different combinations of the two cations which surround the F center octahedrally.[1] No structure of the F band in mixed crystals was found.[3] An additional effect of Schottky defects on the broadening of the F band has been proposed.[5] The lower coloration of mixed crystals has been explained by assumption of higher instability of F centers.[6]

In our general study of crystal defects we undertook a more systematic investigation of color centers in mixed crystals. The selected systems were KCl-RbCl, KCl-KBr, and KBr-RbCl, thus exchanging cations or anions only, or both simultaneously. All three systems form complete solid solutions. The influence of composition, coloration dose, and temperature on the spectral position, intensity, and half-width of V_1, K, F, F', and M bands was studied.

EXPERIMENTAL PROCEDURES

The starting material was cp grade, dried under vacuum at 100° to 300°C before use. Crystals of about 5 cm diam and 6 cm length have been grown by the pulling technique (pulling rate 0.5 cm/h) in a nitrogen atmosphere. Perfect homogeneity of mixed crystals was obtained only for KCl-KBr at the minimum m.p. with composition 36/64 mole % KCl/KBr. In all others a slight inhomogeneity of at most 2% between top and bottom of the crystal was present as determined by potentiometric titration. Vycor crucibles turned out to be superior to Pt, apparently because the traces of OH were removed by chemical reaction with the crucible walls. Despite very careful handling the mixed crystals invariably cracked, indicating very strong internal stress.[7]

Polished samples ($0.35\times1\times1.5$ cm^3) were inserted in a small portable cryostat which was placed in horizontal position for coloration and in vertical position for absorption measurements. The thickness of crystals was selected so that all electrons were absorbed. Crystals were colored by 3-MeV electrons with 10^5 to 2×10^6 rads from a Van de Graaff generator at 20°, −80° and −190°C. Absorption measurements were taken at temperatures equal to or lower than that of coloration in order to avoid bleaching. Aluminum windows 1 mm thick were used for coloration and Ultrasil silica windows for absorption measurements. The samples were rotated 90 deg in vacuum from coloration to absorption position. For absorption measurements a Beckman spectrophotometer (DK-1) covering the spectral range from 0.175 to 3.5 μ was used.

EXPERIMENTAL RESULTS

The absorption spectra of KCl-RbCl, RbCl-KBr, and KCl-KBr colored at −190°C and measured at

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* Sponsored by the U. S. Air Force and jointly by the Office of Naval Research, and Army Signal Corps, and the Air Force.

[1] R. I. Gnaedinger, J. Chem. Phys. **21**, 323 (1953).

[2] E. Mollwo, Nachr. Ges. Wiss. Göttingen Math.-physik. Kl. 97 (1931).

[3] G. Miessner, Z. Physik **134**, 576 (1953).

[4] G. Miessner and H. Pick, Z. Physik **134**, 604 (1953).

[5] I. Ya. Melik-Gaikazyan and E. K. Zavodskaya, Opt. Spectr. (USSR) **9**, 268 (1960).

[6] I. Ya. Melik-Gaikazyan, M. N. Treskina, and E. K. Zavodskaya, Opt. Spectr. (USSR) **9**, 411 (1960).

[7] A. Smakula, N. Maynard, and A. Repucci, Suppl. J. Appl. Phys. **33**, 453 (1962).

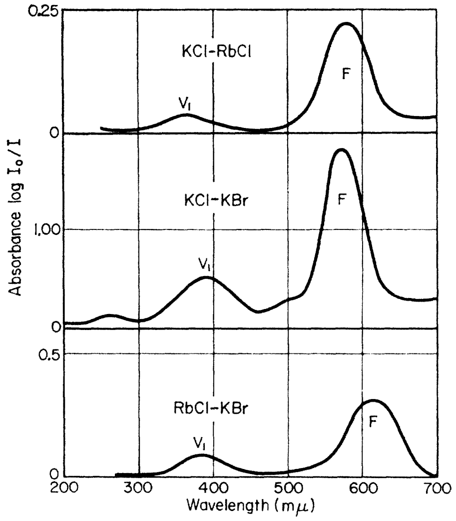

FIG. 1. Absorption spectra of KCl-RbCl, KCl-KBr, and RbCl-KBr mixed crystals colored at −190°C by 3-MeV electrons, 5×10^6 rad, and measured at −190°C.

−190°C show three main bands: V_1 between 300 and 400 mμ, F between 500 and 600 mμ (Fig. 1) and F' between 800 and 1100 mμ (Fig. 2). By exchanging cations (KCl-RbCl) the spectral position of the V_1 band remains almost unchanged while the F band drifts from KCl to RbCl toward lower energy. Replacing anions (KCl-KBr) produces a shift in both the V_1 and F bands. When cations and anions are exchanged simultaneously (RbCl-KBr), only the V_1 band shifts while the F band changes only slightly. The spectral position of the F' band in mixed KCl-RbCl and KCl-KBr is between those of the components but in RbCl-KBr it is at shorter wavelength than in either component.

The shift of the F band with composition is not linear but deviates always toward lower energy (Fig. 3). This deviation is greatest at about 1:1 composition where it reaches 0.03 eV in all three mixed crystals. Figure 3 (top) shows that the energy of the F band in RbCl is lower by 0.02 eV than in KBr. Since the lattice constant of RbCl is 6.58 Å and that of KBr 6.60 Å, the position of the F band violates the Mollwo relation ($\nu d^n =$ const). At 20°C the position of the F band in RbCl is higher than that of KBr by 0.005 eV.

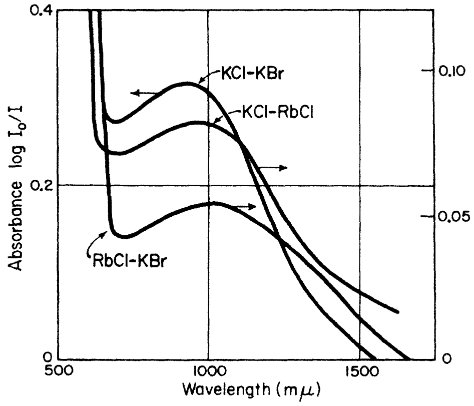

FIG. 2. F' bands of KCl-KBr, KCl-RbCl, and RbCl-KBr mixed crystals colored at −190°C by 3-MeV electrons, 5×10^6 rad, and measured at −190°C.

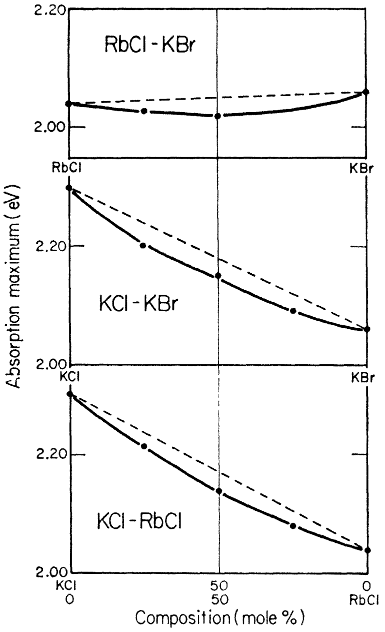

FIG. 3. Influence of composition on spectral position of the F band at −190°C.

The half-width of the F band at −190°C is given in Fig. 4. In pure KCl, RbCl, and KBr, our data are lower than those given by Mollwo,[8] indicating a higher purity and perfection of our crystals. In mixed crystals the

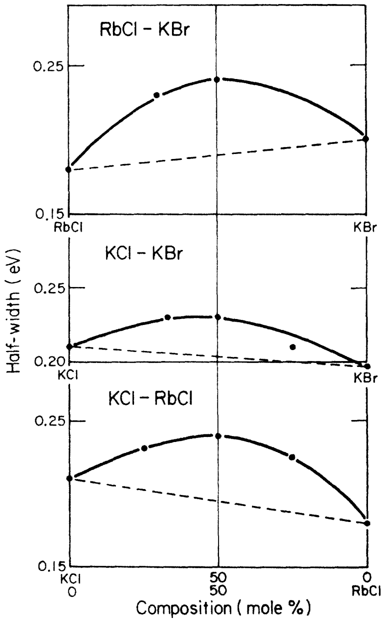

FIG. 4. Influence of composition on the half-width of the F band at −190°C.

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[8] E. Mollwo, Z. Physik 85, 56 (1933).

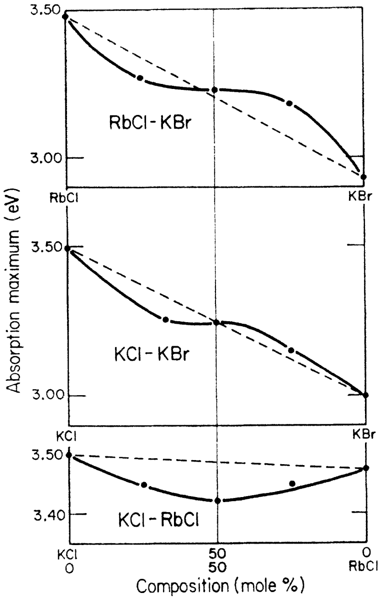

FIG. 5. Influence of composition on spectral position of the V_1 band at −190°C.

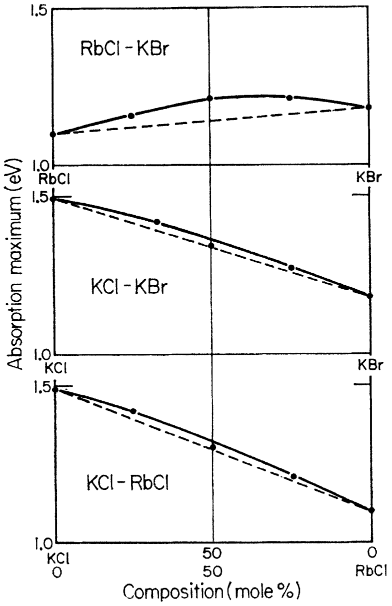

FIG. 7. Influence of composition on spectral position of the F' band at −190°C.

half-width deviation from linearity increases from KCl-KBr → KCl-RbCl → RbCl-KBr.

The behavior of the V_1 band is shown in Fig. 5. In KCl-RbCl the deviation of its spectral position with composition is similar to that of the F band (cf. Fig. 3, bottom). However, the maximum deviation of the V_1 band is more than twice that of the F band although the difference between the V_1 bands in KCl and RbCl is only one tenth of that of the F bands. The spectral position of the V_1 band in KCl-KBr and RbCl-KBr is more complicated than in KCl-RbCl. On the side of KCl- (respectively, RbCl-) rich composition we observe a depletion of the energy and an elevation on the KBr-rich side. At the equimolar compositions the position of the V_1 band corresponds approximately to the arithmetical mean of the respective components.

The half-width of the V_1 band at −190°C in the KCl-KBr system increases similarly to that of the F band, but in KCl-RbCl and RbCl-KBr there is a decrease (Fig. 6).

The nonlinear shift in spectral position of the F' band deviates toward higher energy, contrary to that of the F band (Fig. 7), but only very slightly. According to our measurements the peak of the F' band in KCl is at 825 mμ and that of KBr at 1050 mμ; the corresponding data of Pick[9] are 700 mμ for KCl and 950 mμ for KBr.

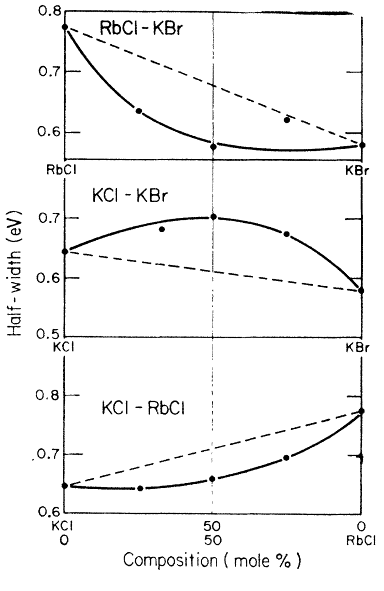

FIG. 6. Influence of composition on the half-width of the V_1 band at −190°C.

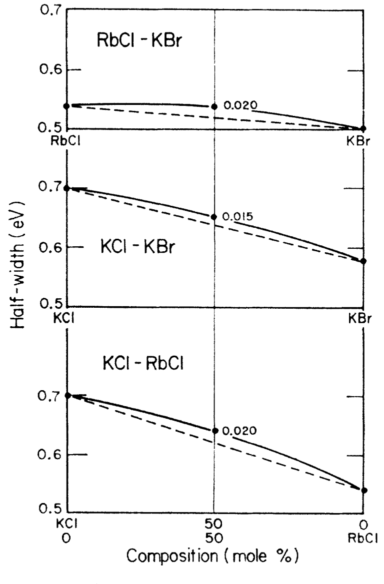

FIG. 8. Influence of composition on the half-width of the F' band at −190°C.

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[9] H. Pick, Ann. Phys. (Paris) 31, 365 (1938).

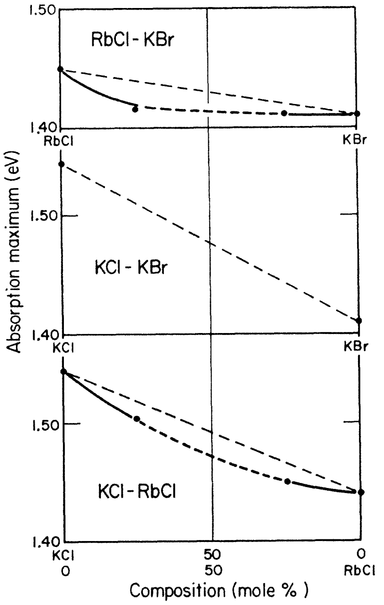

FIG. 9. Influence of composition on spectral position of the *M* band at −190°C.

A direct determination of the half-width of the *F′* band is not possible because of its strong overlap with the *F* band. For comparison we therefore used only the half-width of the low-energy side. Multiplying these values by two we obtain the "apparent symmetrical half-width," which varies between 0.50 and 0.70 eV (Fig. 8). In solid solutions it is only slightly higher than in pure components.

At highest colorations (10^6 rads) at 20°C, *M* bands were formed in addition to the *F* bands. The yield of the *M* bands decreases in solid solutions as the composition approaches 1:1 from either side. Their spectral positions for −190°C are given in Fig. 9. The deviation from linear shift is similar to that of the *F* band.

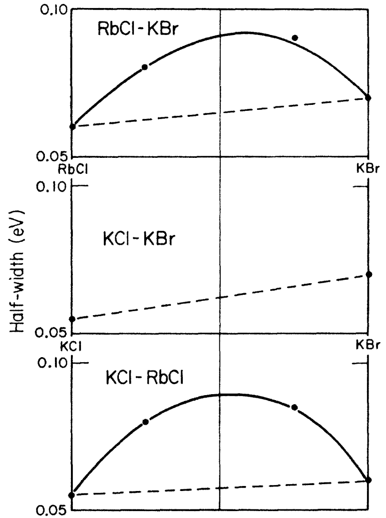

FIG. 10. Influence of composition on the half-width of the *M* band at −190°C.

The broadening of the half-width is also present here (Fig. 10).

In pure KCl and RbCl colored at 20°C and measured at −190°C, *N* bands have been observed at 955 and 1050 mμ. Under the same coloration no *N* bands appeared in solid solutions.

On the high-energy side of the *F* band the *K* band (second excited state of *F*) has always been observed. It is more pronounced in crystals colored at 20°C than at −190°C. The nonlinear spectral shift with composition of the *K* band is toward lower energy, as in the *F* band. Because of a strong overlap with the *F* band, the half-width of the *K* band could be only roughly estimated, similar to that in the *F′* band; it is broader in mixed crystals than in their components.

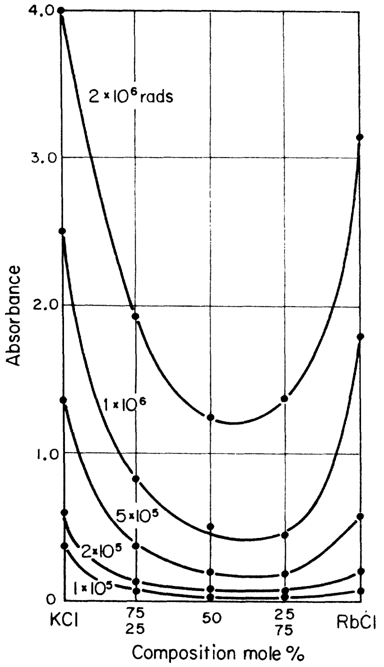

FIG. 11. *F*-center maximum intensity vs composition of KCl-RbCl crystals irradiated (with electrons) and measured at −190°C.

Since the lattice of mixed crystals is always distorted, one expects more defects and therefore higher coloration than in crystals of pure components. This, however, is not the case. The intensities of the *F* bands for various radiation dosages as function of composition are given in Fig. 11 for KCl-RbCl, in Fig. 12 for KCl-KBr, and in Fig. 13 for RbCl-KBr. The *F*-band intensities of KCl-RbCl reach a minimum at 1:1 composition. In KCl-KBr there appears a relative maximum between 60 and 70 mole % of KCl, followed by a relative minimum. One may suspect that lower coloration is caused by higher decay of the *F* band. This effect has been eliminated by keeping the crystals throughout coloration and subsequent measurements at a temperature of −190°C. Repetition of absorption measurements did not disclose any bleaching by the spectrophotometer light source.

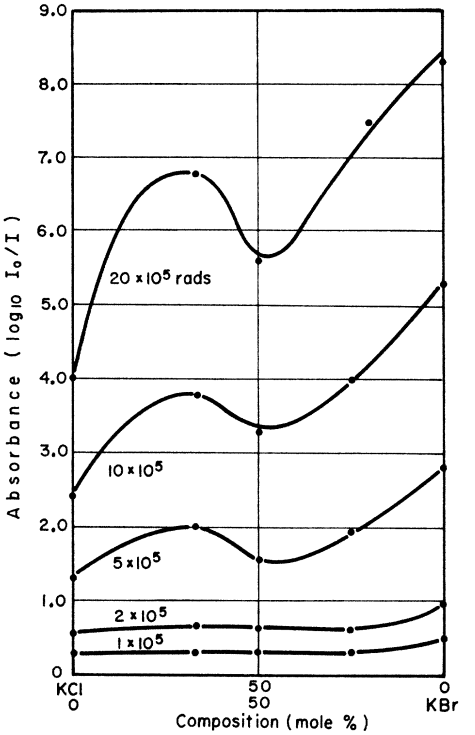

FIG. 12. F-center maximum intensity vs composition of KCl-KBr crystals irradiated (with electrons) and measured at −190°C.

The V_1 and F' bands show similar behavior. Again in KCl-RbCl only a minimum shows up while in KCl-KBr and RbCl-KBr relative maxima and minima appear.

Several absorption bands were observed in the short-ultraviolet region. The position of all observed bands is listed in Table I, and their half-width in Table II.

DISCUSSION

TABLE I. Spectral position of color-center bands of KCl, KBr, RbCl, and KCl-KBr, KCl-RbCl, and RbCl-KBr mixed crystals measured at −190°C.

Designation of center	Composition (mole %)				
	KCl	67–33	50–50	25–75	KBr
N	955ᵃ	. . .	. . .	. . .	. . .
F'	825	875	925	975	1050
M	803ᵃ	. . .	. . .	. . .	880ᵃ
F	540	564	576	595	604
K	465	488	500	525	540
V_1	354	382	383	394	413
V_4	274	265	264	271	275
V_2	237	250	. . .	. . .	230
V_3	. . .	220	220	220	. . .
	190	. . .	195	200	200
	KCl	75–25	50–50	25–75	RbCl
N	955ᵃ	. . .	. . .	. . .	1050ᵃ
F'	825	875	950	1025	1125
M	803ᵃ	825ᵃ	. . .	860ᵃ	858ᵃ
F	540	559	580	598	609
K	465	480	500	520	528
V_1	354	360	363	360	357
V_4	274	. . .	280	. . .	285
V_2	237	235	235	. . .	237
V_3	190	193	207	. . .	210
	. . .	. . .	180	. . .	. . .
	RbCl	75–25	50–50	25–75	KBr
N	1050ᵃ	. . .	. . .	. . .	. . .
F'	1125	1075	1025	1025	1050
M	858ᵃ	879ᵃ	. . .	875ᵃ	880ᵃ
F	609	611	614	610	604
K	528	537	545	545	540
V_1	357	379	384	390	413
V_4	285	280	276	. . .	275
V_2	237	245	. . .	265	. . .
V_3	210	. . .	220	. . .	200

ᵃ Irradiated at room temperature; all others at liquid-nitrogen temperature.

3-MeV electrons with energy doses up to 10^6 rads used in this investigation produce mainly internal ionization in crystals. Atomic displacement is negligible, as proved by repeated coloration. The intensity of repeated coloration after bleaching does not show any marked increase. The coloration produces holes (electron deficiency) and electrons (excess of electrons) in local lattice sites. This primary process does not in practice depend on the kind and properties of the irradiated crystal. The subsequent effects of combination and trapping are, however, very characteristic for each type of crystal.

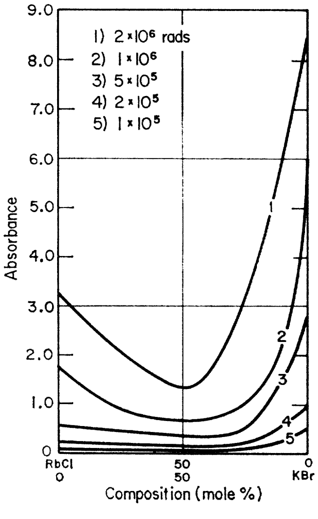

FIG. 13. F-center maximum intensity vs composition of RbCl-KBr crystals irradiated (with electrons) and measured at −190°C.

The F center corresponds to one electron trapped in an anion vacancy. Its spectral position in alkali halide crystals is governed to a first approximation by the interionic distance according to the Mollwo[2]-Ivey[10] relation (νd^n = const). The plot of experimental and theoretical data (Fig. 14) shows considerable deviations not only between theory and experiment but also between the different crystals. At present these deviations[11] cannot be reliably explained.

The ionic distance in mixed crystals changes linearly with composition, but the spectral position of the F

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[10] H. F. Ivey, Phys. Rev. 72, 341 (1947).

[11] A. Smakula, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 729.

TABLE II. Half-widths of color-center bands (eV).

Crystal and composition	V_1 −190°C	K −190°C	F 20°C	F −80°C	F −190°C	F' −190°C	M −190°C
KCl	0.53	···	0.31	···	0.21	0.72	0.055
KCl—RbCl							
75 25	0.66	···	···	···	0.25	···	0.080
50 50	0.68	···	0.37	0.32	0.24	0.64	···
25 75	0.68	···	···	0.28	0.21	···	0.085
RbCl	0.80	~0.30	0.31	0.28	0.18	···	0.060
RbCl—KBr							
75 25	0.64	···	···	···	0.23	···	0.080
50 50	0.57	···	0.42	0.32	0.24	0.54	···
25 75	0.64	···	···	0.33	0.22	···	0.090
KBr	0.58	~0.40	0.35	0.29	0.19	0.58	0.070
KBr—KCl							
75 25	0.66	···	···	···	0.21	···	···
50 50	0.66	···	0.42	0.31	0.23	0.64	···
25 75	0.68	···	···	···	0.23	···	···

band does not. It deviates toward lower energy, reaching a maximum deviation of 0.03 eV for 1:1 composition. The deviation (Fig. 3) is the same whether cations or anion only, or both simultaneously, are exchanged, leading to the assumption that the distortion of the crystalline electric field is the cause of spectral shift. In non-isomorphous crystals, e.g., NaCl-KCl, the observed deviation is much greater, 0.32 eV for 1:1 composition. The *F*-band position at −190°C is at 575 mμ, while in NaCl it is at 450 and in KCl at 550 mμ.

The half-width of the *F* band in mixed crystals parallels the spectral shift (Fig. 4); it increases, reaching a maximum increase of about 25% at 1:1 composition. In non-isomorphous NaCl-KCl it is much greater, about 1 eV. The *F*-band broadening is evidently due to the same cause as the spectral shift.

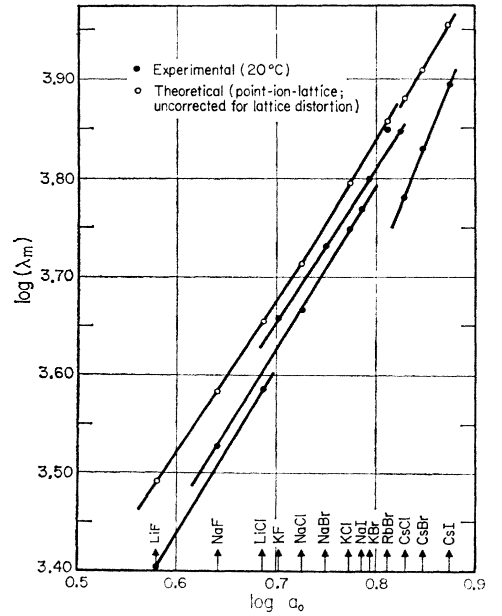

FIG. 14. Spectral position of *F* centers as a function of interionic distance (Mollwo-Ivey relation).

The intensity of the *F* band depends on the concentration of anion vacancies in the crystals. The computed *F*-center concentration was 3×10^{14} to 6×10^{16} centers/cm^3 for the radiation dose 10^5 to 10^6 rad. The concentration of anion vacancies must be higher than that of *F* centers, since a saturation of coloration has been not reached. As has been stated before, the formation of anion vacancies during the electron bombardment was negligible. On the other hand a decay of *F* centers has been prevented by keeping the crystals at low temperature. The lower coloration of KCl-RbCl and RbCl-KBr may be caused either by a smaller concentration of anion vacancies or by a smaller capture cross section. A decrease of anion vacancies is unlikely; a decrease of trapping caused by lattice distortion seems more probable.

The more complicated intensity change in KCl-KBr (Fig. 12) indicates that solid solutions might not be completely random at all compositions. The relative maximum in KCl-KBr, which occurs at about 65 mole % of KCl, coincides with the minimum m.p. (the KCl-RbCl and RbCl-KBr solid solutions do not have a minimum m.p.).

The *K* center is considered to be a second excited state of the *F* electrons.[12] It is located on the high-energy side of the *F* band and strongly overlapped by it. It always appears together with the *F* band. In KCl, RbCl, and KBr crystals colored at 20°C and measured at −190°C, the peak of the *K* band was always more pronounced than in crystals colored at −190°C, while in mixed crystals there was no difference between crystals colored at 20° and −190°C. Assuming symmetry of the *F* band, the *K* band seems to be asymmetrical. The deviation of spectral shift with composition is toward lower energy, as in the *F* band. The half-width and the intensity of the *K* band are uncertain because of the strong overlap by the much more intense *F* band.

The *M* center is a pair of *F* centers in the closest face-

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[12] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, (Clarendon Press, Oxford, 1940).

diagonal position.[13] It appears only at 20°C coloration. The spectral shift and the deviation from linearity with composition is the same as in the *F* band. The half-width of the *M* band is much smaller than that of the *F* band but the relative influence of the composition is stronger. The intensity of the *M* band is directly proportional to the square of the *F*-band intensity. It was impossible to detect the *M* band at 1:1 composition of all three solid solutions for electron doses up to 2×10^6 rad. The *N* band showed similar behavior; it appeared only in pure components but not in solid solutions.

The *F′* center corresponds to two electrons in one anion vacancy. It appears only at −190°C coloration together with the *F* band. The spectral position in pure KCl and KBr has been reported by Pick[9] to be at 700 and 950 mμ, respectively. According to our measurements the maxima are at 825 mμ for KCl and at 1050 mμ for KBr. This difference is much too large for experimental error; it is probably caused by the different processes of *F′*-center formation. In our case the *F′* centers were formed during irradiation, while Pick's were formed by subsequent photochemical decomposition of the additively formed *F* centers. In his case some additional centers on the low-energy side of the *F′* band are probably formed and overlap with the *F′* band, causing the apparent shift. The deviation of the spectral position from linearity with composition is here toward higher energy, as opposed to that of the *F* band. It is, however, quite small. The shift is probably due to the weakening of repulsion between the two electrons. The half-width in mixed crystals is slightly higher than in pure components.

The intensity change of the *F′* band with composition is basically similar to that of the *F* band, but less pronounced. The intensity ratio of $F:F'$ varies between 28 at low coloration and 5 at high coloration. Crystals colored at 20°C (no *F′* band) and subsequently at −190°C show much stronger *F′* bands than those colored at −190°C only, indicating that electrons produced by the coloration are trapped directly at the *F* centers.

From electron spin resonance, Castner and Känzig[14] assumed that the V_1 center is a halogen-molecule ion located in a space of two anions along the face diagonal in the lattice. However, subsequent work showed that the structure of V_1 center is uncertain.[15,16] It is one of the electron-deficient centers. It is formed at −190°C only. The shift of the spectral position with composition is similar to that of the *F* band in KCl-RbCl. In KCl-KBr and RbCl-KBr, however, the shift is irregular. An excess of Cl ions depresses while the Br ions enhance the spectral energy position. This irregularity is probably connected with the three types of possible molecule ions: Cl_2^-, $(ClBr)^-$, and Br_2^-. The irregularity of the shift can be explained by a combination of these molecule ions.

The half-width of the V_1 band in KCl-KBr changes with composition, same as that of the *F* band. In KCl-RbCl and RbCl-KBr, there is a decrease of the half-width. This apparent difference may be caused by superposition of other *V* bands, which may be hidden. However, the decrease of the half-width is symmetrical on both sides of the maxima, requiring the disappearance of two additional bands; this, however is improbable. A proper explanation of the half-width decrease cannot be provided at present.

The intensity change of the V_1 bands with composition is again the same as in the *F* band but less pronounced.

Several bands have been observed below 350 mμ. A tentative correlation of three of them to V_2, V_3, and V_4 according to Dorendorf's nomenclature[17] is given in Table I. Some other bands either did not appear in all crystals or did not agree with Dorendorf's data; they might be more dependent on composition or defects than the bands at lower energies.

Our results show that the interaction between the trapped electrons or holes and crystal structure is quite complicated. Further study is necessary before a real understanding will be possible.

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[15] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids 9, 70 (1958).

[16] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. 121, 1043 (1961).

[17] H. Dorendorf, Z. Physik 129, 317 (1951).