

Ultraviolet Absorption of KI Diluted in KCl Crystals*†

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The absorption of KI diluted in KCl single crystals was studied for concentrations of 10^{-3} to 10^{-5} mole fraction KI in the temperature range from 80°K to 700°K. The exact shape of the long-wavelength absorption peak, which is Gaussian around the maximum and exponential at the edge, was measured quantitatively over four orders of magnitude. The total integrated absorption is proportional to the iodide concentration which was determined chemically. In the limit of high temperatures the half-width of the band is proportional to the square root of the temperature and the edge follows Urbach's law. Deviations at low temperatures were shown to arise from zero-point oscillations. The results were compared with models for localized excitons.

INTRODUCTION

THE first exciton band of pure alkali halides, for example KI, has been studied in great detail with samples cleaved from single crystals at low absorption levels at the long-wavelength edge of this band.¹ Around the band maximum only the optical density which is a relative measure of the absorption constant could be investigated, because the high absorption constant of the band maximum requires that the measurements are taken with thin evaporated films.² On the other hand, the *F* band in alkali halides, for example in KCl, has been studied quantitatively in great detail around the band maximum.³ Lower absorption levels have, however, not been measured, because of the overlap of other centers and because of the fact that the light used in the absorption measurements bleaches the *F* centers. A complete, quantitative study of an optical absorption line in alkali halides over its entire range of many orders of magnitude would thus contribute to the understanding of the broadening of absorption lines by electron-phonon interaction.

By adding 1% KI to a KCl crystal, Smakula and Hilsch and Pohl⁴ showed that an additional absorption due to diluted KI can be observed in the transparent region of KCl. This suggested that it would be possible to study the complete absorption spectrum of the I⁻ absorption by diluting KI in KCl and measuring the optical absorption spectrum of these mixed crystals. In the present work, the shape, the concentration dependence, and the temperature dependence of the KI absorption was measured quantitatively by this

method. During the course of the present work Uchida *et al.*⁵ reported measurements of the KI absorption in KCl at room temperature and liquid nitrogen temperature for a crystal containing 5×10^{-4} molar fraction KI.

CRYSTAL PREPARATION

The mixed crystals were grown in the [100] orientation in a Kyropoulos furnace with an atmosphere of purified argon. A graphite beaker was used to melt reagent-grade KCl powder (Mallinckrodt Chemical Works), previously heated in a chlorine atmosphere.⁶ KI was added to the melt in a mol ratio of 5×10^{-3} to 5×10^{-5} . The growth rate of the crystals was 0.5 mm/min. From a typical boule, sketched in Fig. 1(a) samples were taken along the axis of growth at positions

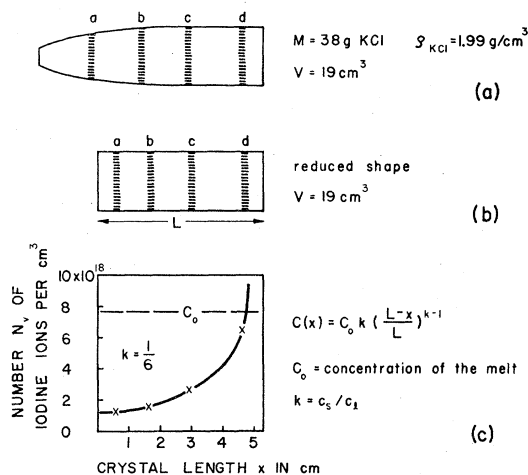


FIG. 1. Distribution of the iodide concentration in KI:KCl mixed crystals. Samples were taken along the axis of growth at positions *a*, *b*, *c*, and *d*. (a) Sketch of the boule as grown. (b) Sketch of the boule, normalized to uniform cross section. (c) Distribution of the iodine concentration along the axis of the boule, normalized to uniform cross section.

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† A preliminary report of the present work was given at the Monterey meeting of the American Physical Society, March, 1961 [Bull. Am. Phys. Soc. 6, 114 (1961)].

¹ U. Haupt, Z. Physik 157, 232 (1959).

² W. Martienssen, J. Phys. Chem. Solids 2, 257 (1957); Nachr. Akad. Wiss. Göttingen, Math.-phys. Kl. IIa 11, 257 (1955); K. J. Teegarden, Phys. Rev. 108, 660 (1957); J. E. Eby, J. K. Teegarden, and D. B. Dutton, *ibid.* 116, 1099 (1959).

³ J. D. Konitzer and J. J. Markham, J. Chem. Phys. 32, 843 (1960); G. A. Russell and C. C. Klick, Phys. Rev. 101, 1473 (1956); E. Mollwo, Z. Physik 85, 56 (1933).

⁴ A. Smakula, Z. Physik 45, 1 (1927); R. Hilsch and R. W. Pohl, *ibid.* 57, 145 (1929).

⁵ K. Nakamura, K. Fukunda, R. Kato, A. Matsui, and Y. Uchida J. Phys. Soc. Japan 16, 1262 (1961); K. Fukunda, R. Kato, K. Nakamura, and Y. Uchida, *ibid.* 15, 1344 (1960).

⁶ The author wishes to acknowledge the help of the Farbwerke Hoechst AG, Frankfurt, Germany, for kindly providing the chlorine resistant vacuum grease "Hostafon" which was essential for this treatment.

a, *b*, *c*, and *d*. The iodine content of these samples was determined by a special colorimetric chemical analysis.⁷ In Fig. 1(c) the concentration of iodine ions is plotted vs the position of the samples along the length of the boule. In this plot the abscissa was normalized to uniform crystal cross section as indicated in Fig. 1(b). The concentration of iodine varies with the position, especially at the end of the crystal; at the earliest stages of crystal growth, the concentration of the iodine ions in the crystal is only 1/6 of the concentration in the melt. The data fitted Pfann's formula⁸ for "normal freezing" and gave a segregation coefficient $k=1/6$. This result for KI may be compared with a value of almost unity, which Kobayashi and Tomiki⁹ obtained for the segregation coefficient of Br^- in KCl with a comparable growth rate. This might indicate a dependence of the segregation coefficient in KCl on the ion size of the added impurity. We may also compare this behavior with the fact that KBr forms a continuous range of solid solutions with KCl whereas KI and KCl form a eutectic phase in thermal equilibrium at higher KI concentrations.

EXPERIMENTAL TECHNIQUE

The absorption constant of KI in KCl varies over many orders of magnitude; thus, to assure a reasonable transmitted light intensity, samples of widely differing thicknesses had to be used. Down to thicknesses of 0.2 mm, the specimens were prepared by cleavage, while thinner specimens were obtained by melting small pieces of the mixed crystals between two parallel quartz plates. The thickness of these thinner crystalline plates was determined by weighing. It was found that these crystal plates do not differ in their optical behavior from single crystals.

At room temperature and liquid nitrogen temperature the absorption constants were measured in a vacuum ultraviolet monochromator having a resolution of about 0.015 eV. This resolution permitted an accurate determination of a rapidly changing absorption constant, since in each case the logarithm of the transmitted light intensity was found to be inversely proportional to the sample thickness. Above room temperature some measurements were made with a Cary spectrophotometer model 14 fitted with a special accessory to allow measurements up to 500°C. The resolution of this instrument was much worse and therefore corrections were made for the larger slit width. Following an analysis of Urbach and Moser¹⁰ only data points with $Kd=1$ were used for each sample. Reflection losses were minimized by comparing

the ratio of the transmitted light intensity of two crystals of different thicknesses.

EXPERIMENTAL RESULTS

The absorption constant at room temperature for various concentrations of KI is shown in Fig. 2. The three upper curves show the result of three mixed crystals containing 1.3×10^{19} , 1.4×10^{18} and 1.7×10^{17} iodine ions/cm³. The two lower curves were obtained from pure crystals of KCl. At short wavelengths the steep rise of the edge of the first exciton peak of the host KCl limits the range of observation. Clearly

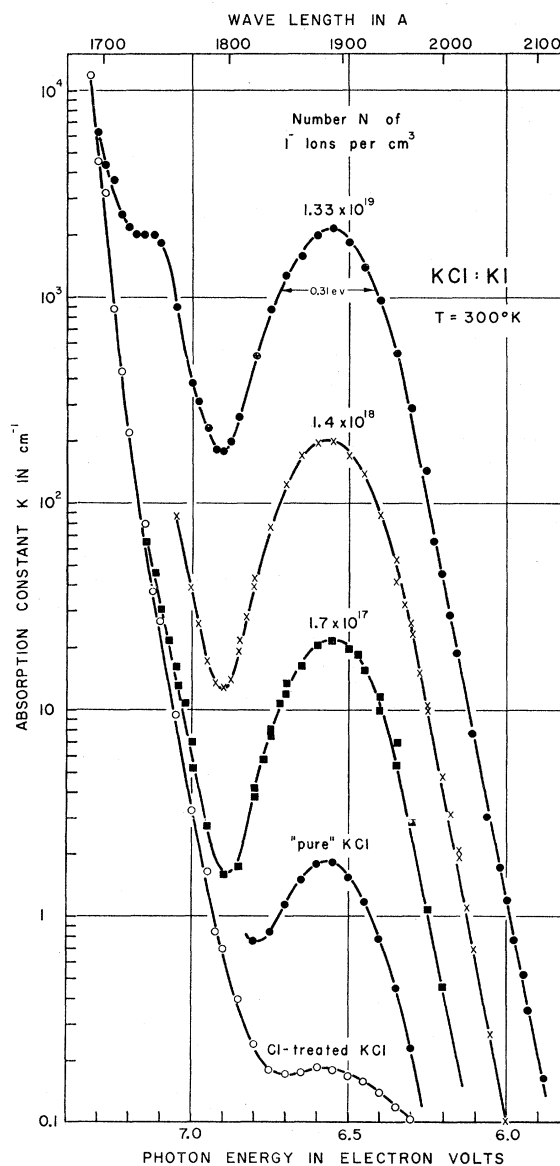


FIG. 2. KI absorption bands in KCl at room temperature for various iodine concentrations. The iodine concentration for the three mixed crystals is as indicated. The two lower curves were obtained from pure KCl.

⁷ F. G. Houston, *Ann. Chem.* **22**, 493 (1950).

⁸ W. G. Pfann, *Zone Melting* (John Wiley & Sons, Inc., New York, 1958).

⁹ K. Kobayashi and T. Tomiki, *J. Phys. Soc. Japan* **15**, 982 (1960).

¹⁰ F. Urbach, *Phys. Rev.* **93**, 1324 (1953); F. Moser and F. Urbach, *ibid.* **102**, 1519 (1956).

resolved from it, an absorption band due to diluted KI is seen. The position of the absorption maximum is 6.57 eV and the half-width of the peak is 0.31 eV for each of the KI concentrations measured.

These absorption peaks may be normalized and superposed upon a common curve, having a Gaussian distribution around the maximum absorption (solid line in Fig. 3) and an exponential edge at the long-wavelength side (dashed line in Fig. 3). The data points correspond to the three mixed crystals of Fig. 2.

In Fig. 4 the total integrated absorption $\int K d(h\nu)$ of the band is plotted vs the KI concentration for the mixed crystals. Over a wide range of concentrations the total integrated absorption is proportional to the KI concentration. For pure KI the only quantitative determination of the absorption constant was done in 1934 by Bauer.¹¹ The total integrated absorption for

pure KI calculated from his measurements is also given in Fig. 4. This value is lower than the extrapolated value for diluted systems by a factor of 3.6.

The two lower curves of Fig. 2 were obtained from pure KCl crystals. The crystal giving rise to the lowest absorption curve was grown from chlorine treated reagent-grade KCl. From its residual absorption a concentration of about 10^{15} iodine ions/cm³ was extrapolated from Fig. 4. The "pure" crystal, grown from untreated reagent-grade KCl contains a factor of 10 more KI impurities. It thus appears that chlorine treatment is very effective in removing iodide impurities in KCl. In both cases the specimens were taken from the enriched end of the boules. The initial growth contains approximately a factor of 5 less KI.

The temperature dependence of the 6.57-eV KI absorption peak and its long-wavelength edge is shown in Fig. 5 for samples containing about 10^{-3} molar fraction KI. While the half-width of the band increases, the position of the maximum and the edge shift to lower photon energies with increasing temperature. Plotting the half-width vs the temperature in Fig. 6, we find that above room temperature the half-width is proportional to the square root of the temperature. At lower temperatures the half-width approaches a constant value.

The total integrated absorption was determined from Fig. 5 and is summarized in Table I for various temperatures.

A second absorption band at 7.14 eV with a half-width smaller by a factor of 2 than that of the first band is resolved at the highest KI concentration

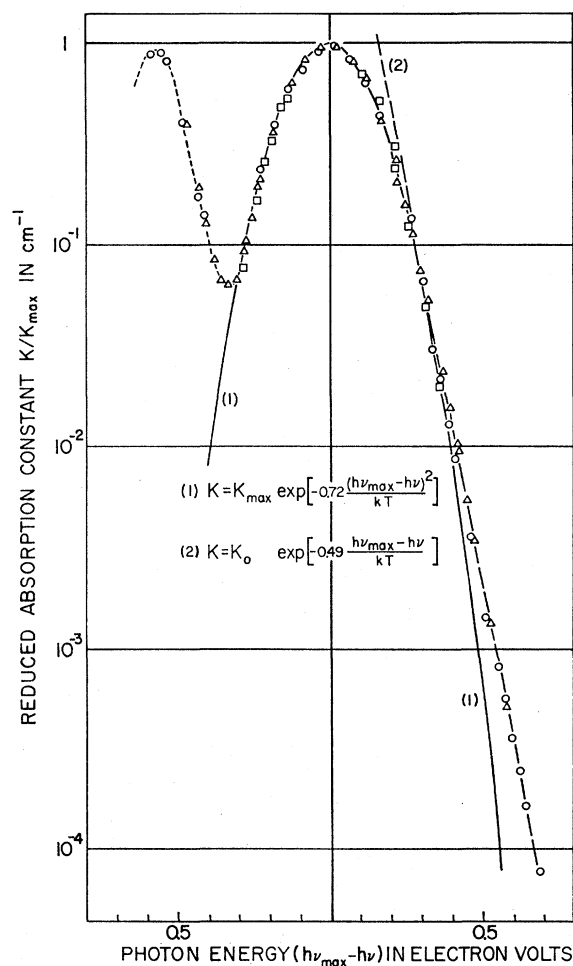


FIG. 3. Normalized common curve of the long-wavelength KI absorption band for three mixed crystals: \circ , 1.3×10^{18} ; Δ , 1.4×10^{18} and \square , 1.7×10^{17} iodine ions/cm³. The solid line represents a Gaussian, the dashed line an exponential distribution.

¹¹ G. Bauer, Ann. Physik 5, 19, 434 (1934).

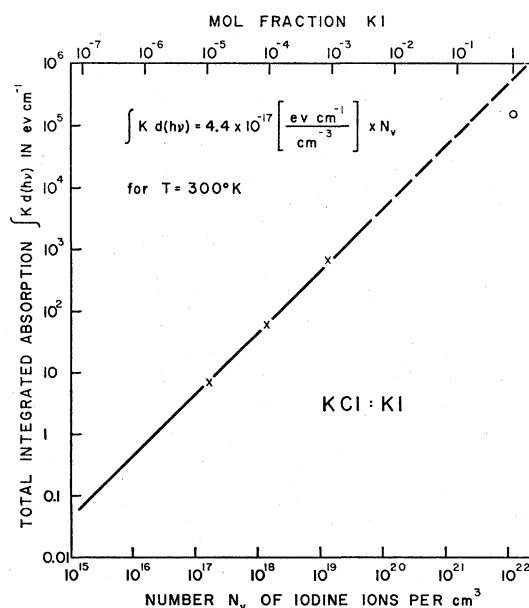


FIG. 4. Total integrated absorption of the KI band vs the iodine concentration at room temperature. The circle symbol indicates the value of the total integrated absorption for pure KI as calculated from measurements of Bauer.

(Fig. 2). This peak is more prominent at liquid nitrogen temperature. It was found, however, that the temperature shift of this band is much less than the shift of the first band.

INTERPRETATION OF THE RESULTS

Band Shape

The following observations indicate that the iodine ions are atomically dispersed in the KCl lattice: (1) The half-width of the absorption band is small; (2) no colloidal bands were found at longer wavelengths; (3) the total integrated absorption is proportional to the KI concentration. Since the position of the band, its half-width, and its shape were found to be independent of the KI concentration, we conclude that the interaction between neighboring KI centers is negligible and that we can associate the observed band with localized electron transitions at isolated KI centers. This localized exciton band of dilute KI in a KCl matrix is shifted from the position of the first exciton

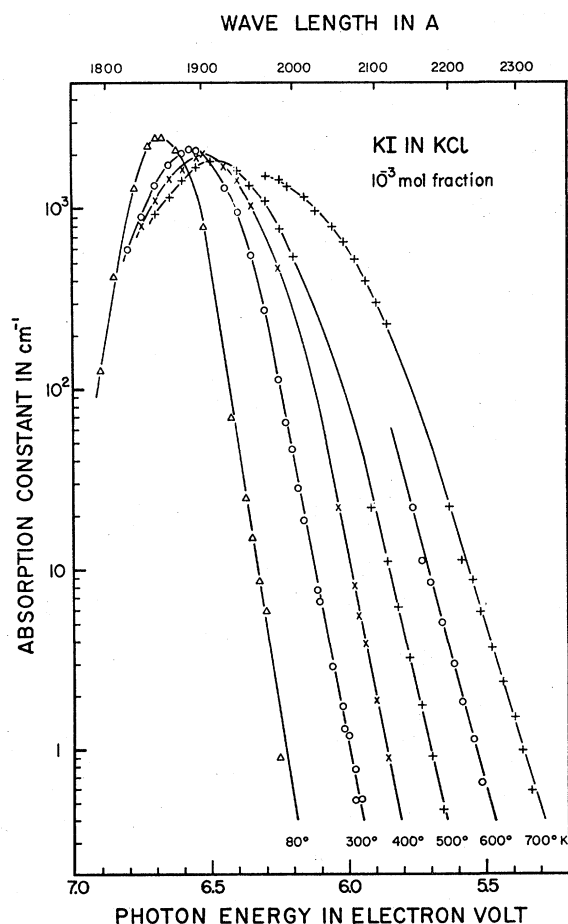


Fig. 5. Temperature dependence of the KI absorption band for samples containing about 10^{-3} molar fraction KI.

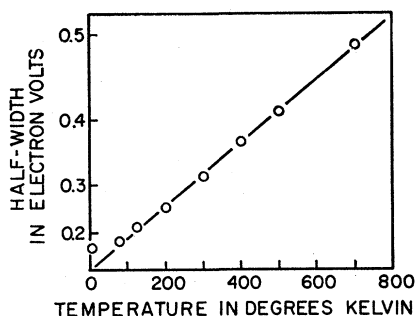


Fig. 6. Half-width of the KI band for various temperatures. For the ordinate a quadratic scale is used.

peak in pure KI. A previous investigation¹² has shown, however, that a similar shift of the first exciton peak of KBr diluted in KCl could be related to a change in lattice constant due to the mixing.

If there is no interaction between absorption centers, the broadening of the absorption band is caused by lattice vibrations. At isolated absorption centers the displacement of the surrounding ions can be described by a set of effective normal modes. Stimulated by the *F*-center problem, a number of different approaches have been made to deal with the broadening of an optical absorption line by electron-phonon interaction. Markham¹³ has given a comprehensive review of different approximations. We do not want to go into the details of different assumptions about local modes and the use of more rigorous quantum-mechanical methods. A very careful comparison of the shape of the *F* band in KCl and NaCl by Konitzer and Markham³ shows than an enormous number of detailed measurements of the band shape, especially at low temperatures, and a large number of numerical calculations have to be carried out before a decision can be made about the validity of special models. This detailed knowledge which would have to include the short-wavelength edge as well as emission data, is not yet available for the iodine center in KCl. Here we shall consider only the simplest model which assumes that the broadening of the *I*⁻ band around the band maximum is caused by one or several local modes of the same frequency, interacting with the electron transition from the

TABLE I. Total integrated absorption of the KI absorption band at various temperatures for 10^{-3} molar fraction KI.

Temperature (°K)	Total integrated absorption (ev cm ⁻¹)
80	605
300	725
400	785
500	810
700	795

¹² H. Mahr, Phys. Rev. **122**, 1464 (1961).

¹³ J. J. Markham, Revs. Modern Phys. **31**, 956 (1959).

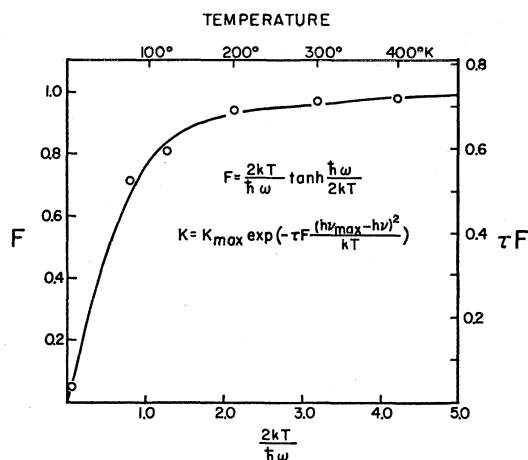


FIG. 7. The constant τF of the Gaussian distribution of the absorption constant around the maximum determined from the half-width of the bands is plotted vs the temperature (right and upper scales). The correction function F (solid line) can be best fit for $\hbar\omega = 16 \times 10^{-3}$ ev and $\tau = 0.75$ ev $^{-1}$ (see left and lower scales).

ground state to the excited state at the iodine center. The total energy of the center can then be described in terms of a single configurational coordinate q with parabolic energy curves for the ground and the excited state. The energy difference ΔE for the electronic transition then becomes a quadratic function of the "effective" displacement q of the surrounding ions:

$$\Delta E \sim Aq + Bq^2. \quad (1)$$

Band shape around the band maximum. Around the band maximum the quadratic term of formula (1) may be neglected, either because of the small ion displacement involved or because the vibrational modes of ground and excited state are equal ($B=0$). We then derive a Gaussian function of the absorption constant around the band maximum using a semiclassical Franck-Condon picture with a one-coordinate oscillator model¹⁴:

$$K = K_{\max} \exp[-\tau F(\hbar\nu_{\max} - \hbar\nu)^2/kT], \quad (2)$$

where K_{\max} is the maximum absorption constant, $\hbar\nu_{\max}$ is the position of the band maximum, and τ is a constant. The function $F = (2kT/\hbar\omega) \tanh(\hbar\omega/2kT)$ extends the Boltzman probability distribution of a classical oscillator to low temperatures where zero-point oscillations of a quantum-mechanical oscillator become important.

For a comparison of the results around the band maximum with formula (2), we determine the constant τF from the half-width of the bands in Fig. 5 and plot it vs the temperature in Fig. 7. We fit τF to a solid line representing $F = (2kT/\hbar\omega) \tanh(\hbar\omega/2kT)$. From a

best fit we obtain $\hbar\omega = 16 \times 10^{-3}$ ev ($\nu = 3.9 \times 10^{12}$ sec $^{-1}$) and $\tau = 0.75$ ev $^{-1}$. From a similar analysis, Russell and Klick³ and more recently Konitzer and Markham³ found $\nu = 3 \times 10^{12}$ sec $^{-1}$ for the F center in KCl. If we compare these values with calculations of the vibrational spectrum of pure KCl by Karo¹⁵ we find that these modes lie within the phonon bands of the host KCl. It might well be, therefore, that a single frequency obtained from the above analysis represents the weighted influence of many lattice modes to the band broadening.

Band shape at the long-wavelength edge. The absorption constant at the long-wavelength edge of the iodine absorption band in KCl varies exponentially over many orders of magnitude (Figs. 2, 3, and 5). This exponential rise at the long-wavelength edge of several solids is known as Urbach's¹⁰ law:

$$K = K_0 \exp[-\sigma(\hbar\nu_0 - \hbar\nu)/kT], \quad (3)$$

where K_0 , σ and $\hbar\nu_0$ are constants. This law holds for pure KBr,¹⁶ KI,¹ and KCl¹⁷ over as much as six orders of magnitude of the absorption constant K . Moreover, the constant σ was found to be $\sigma = 0.80 \pm 0.02$ in all these substances. It has also been found in KBr¹⁶ and KI¹ that Urbach's rule (3) breaks down at low temperatures. The absorption constant still rises exponentially with $\hbar\nu$, but the constant σ has a different value. This was attributed to the influence of zero-point oscillations at these temperatures.^{1,16}

We might therefore extend Urbach's rule to include low-temperature measurements by using the same correction function F which describes the influence of zero-point vibrations around the band maximum:

$$K = K_0 \exp[-\sigma F(\hbar\nu_{\max} - \hbar\nu)/kT]. \quad (4)$$

This modified Urbach rule (4) shall now be compared with the experimental results, obtained at the long-wavelength edge. We determine the constant σF from the slope of the edges in Fig. 5 and plot σF vs the temperature (Fig. 8, right-hand upper scale). The solid curve represents the quantum-mechanical correction function $F = (2kT/\hbar\omega) \tanh(\hbar\omega/2kT)$ (left-hand scale). Adjusting the two parameters $\hbar\omega$ and σ for a best fit we obtain $\hbar\omega = 60 \times 10^{-3}$ ev which corresponds to a vibrational frequency of $\nu = 14.5 \times 10^{12}$ sec $^{-1}$. The value of σ is 0.77, very close to the value $\sigma = 0.80 \pm 0.02$ found for the pure alkali halides. It thus appears that the exponential rise expressed in formula (4), seems to be peculiar to the exciton state in alkali halides with the constant σ being independent of the nature of the absorbing ions. For higher temperatures the results approach Urbach's law which is formula (4) when $\hbar\omega \ll kT$ (F approaches 1 in this case). In Fig. 9

¹⁴ M. Lax, J. Chem. Phys. **20**, 1752 (1952); C. C. Klick and J. H. Schulman, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5; D. L. Dexter, *ibid.* Vol. 6.

¹⁵ A. M. Karo, J. Chem. Phys. **33**, 7 (1960).

¹⁶ W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).

¹⁷ K. Kobayashi and T. Tomiki, Technical Report ISSP, Ser. A No. 19, 1961, Tokyo, Japan (unpublished).

the exponential distribution of the absorption constant at the edge is extrapolated. Above 500°K, Urbach's law holds with one unique set of constants σ , K_0 , and $h\nu_0$, where $K_0 = 5 \times 10^6 \text{ cm}^{-1}$ for these samples containing 10^{-3} mole fraction KI. Assuming a linear dependence of K_0 on the concentration of absorbing centers the latter value agrees well with $K_0 = 6 \times 10^9 \text{ cm}^{-1}$ found for pure KI.¹ Kobayashi and Tomiki¹⁷ reported $\sigma = 0.51$ for localized excitons due to diluted KBr in KCl in the temperature range from 300° to 470°K. Their value agrees with an average value found for diluted KI in the present work within this temperature range. For pure alkali halides the corrections due to zero-point oscillations set in only at very low temperatures. As a measure of the range of classical statistics we define an effective temperature¹⁴ $T_{\text{eff}} = (\hbar\omega/2k) \coth(\hbar\omega/2kT)$ and get $T_{\text{eff}} = 360^\circ\text{K}$ for the KI band in KCl, compared to 60° to 80°K found for pure¹⁶ KBr and ¹KI.

Discussion. The experimental results of the band shape of the I^- band in KCl can be analytically described by a Gaussian function around the band maximum and an exponential function of the absorption constant at the long-wavelength edge. Simple one-coordinate models using the semiclassical Franck-Condon principle do not explain these results over the whole range. Rigorous quantum-mechanical treatments of the problem have not been carried to the point where a complete description of the band shape is given over the whole range, that is, including also very small absorption constants at the tails of the band.

Two proposals seem promising in explaining the results obtained for the iodine center in KCl. One model^{13,18} assumes that the modes interacting with the electronic transition are independent of the

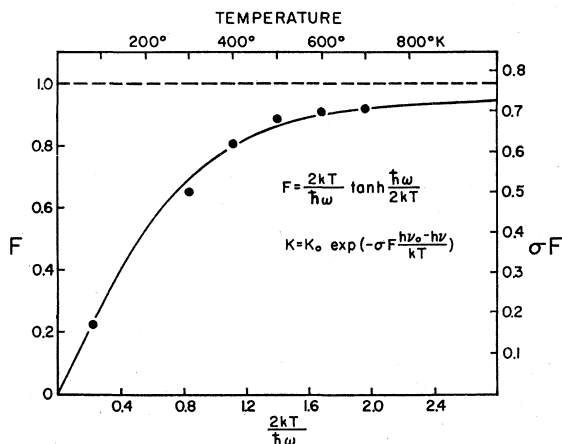


FIG. 8. The constant σF of the exponential distribution of the edge of the KI band plotted vs the temperature (right and upper scales). The correction function F (solid line) can be best fitted by the data for $\hbar\omega = 60 \times 10^{-3} \text{ eV}$ and $\sigma = 0.77$ (see left and lower scales.)

¹⁸ We appreciate very much that M. Wagner pointed out the consequences of this model previous to the publication which will appear in *Z. Naturforsch.*

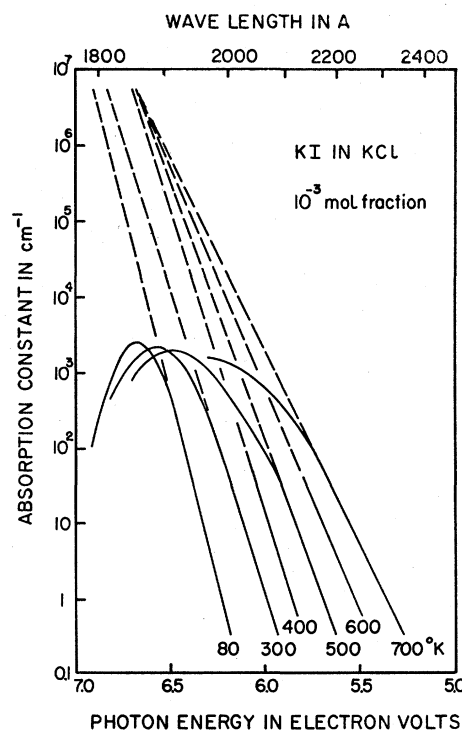


FIG. 9. Temperature dependence of the KI absorption band. The exponential rise of the absorption constant at the long-wavelength edge has been extrapolated.

electronic state. This is equivalent to assuming that the energy difference for the transition is linearly dependent on the ionic displacements. In this many-mode case, a closed form for the band shape can be derived for certain portions of the absorption curve. One obtains a slightly asymmetric Gaussian curve around the band maximum and an exponential approximation for lower photon energies. Wagner is currently trying to fit the experimental results to the predictions of this model.

Another model, suggested by Toyozawa,¹⁹ also assumes that at least two modes are interacting with the center. While for one mode (a longitudinal accoustical mode) the oscillator frequency should be independent of the electronic state, it is assumed that the second mode (either a longitudinal optical or a transverse accoustical mode) is strongly dependent on the electronic state. Therefore, quadratic terms in the ionic displacements will be predominant for the second mode, whereas a linear dependence on q is assumed for the first mode. A further analysis has not been carried out, but qualitatively an exponential dependence of the absorption constant on $h\nu$ can be expected for low absorption levels at the edge of the band.

The interpretation of a vibrational mode, obtained

¹⁹ Y. Toyozawa, *Progr. Theoret. Phys. (Kyoto) Suppl. No. 12*, 111 (1959).

from a best fit of the experimental results to formulas (2) and (4) remains difficult. In both cases, the experimentally determined frequency might be an effective mode describing the averaged influence of many modes. The question of how many modes are interacting with the center is closely related to the problem of a careful comparison of the band shape with the predictions of specific models. As this analysis has not been done, formulas (2) and (4) with a single mode are still a useful way of describing experimental results.

Total Integrated Absorption

Dexter,²⁰ as well as Lax and Herring,²¹ calculated the total integrated absorption due to localized absorption centers in dilute systems:

$$\int Kd(h\nu) = 1.1 \times 10^{-16} [\text{cm}^3/\text{ev}^{-1} \text{cm}] \times (1/n)(E_i/E_0)^2 f N_0, \quad (5)$$

where n is the index of refraction of the host KCl at the band maximum of the KI peak, E_i/E_0 the local field correction, f the oscillator strength of the electron transition *in vacuo*, and N_0 the concentration of absorbing centers. We calculate the oscillator strength f from the linear dependence of the total integrated absorption on the iodide concentration (Fig. 4). f equals 0.24 with the use of the Lorentz-Lorenz field correction $E_i/E_0 = (n^2 + 2)/3$ and $n = 1.8$.²² This value of the oscillator strength is a lower limit for the localized exciton transition at diluted KI centers in KCl, because the Lorentz field is an overestimation of the actual field at the impurity center. After completion of this work, Ishii²³ reported independently the oscillator strength f for the iodine band in KCl. Using Smakula's original equation which assumes a Lorentzian shape of the band, he finds $f = 0.30 \pm 0.04$. This value agrees within the limits given with our value, if f is calculated

from the same formula in both cases. Heer and Rauch²⁴ determined $f = 0.31$ for F centers in pure KI, using the Lorentz-Lorenz field.

The slight increase of the total integrated absorption with temperature (Table I) might be due to a variation of the index of refraction of the host KCl. Only the room temperature values of n have been measured so far.²² Generally, however, the index of refraction decreases with decreasing temperature at the edge of an absorption band. The dispersion curve sharpens as well as the absorption band itself.

SUMMARY

(1) KI diluted in single crystals of KCl gives rise to two absorption bands which are not hidden in the host KCl absorption. Their positions are 6.57 and 7.14 eV at room temperature.

(2) The shape of the long-wavelength band was found to be Gaussian around the band maximum, whereas the distribution of the absorption constant at the long-wavelength edge of the band was exponential.

(3) Position and half-width of the band are independent of the KI concentration in the range of 10^{-3} to 10^{-5} molar fraction KI in KCl. The total integrated absorption is proportional to the KI concentration in the same range.

(4) At higher temperatures the half-width of the band is proportional to $T^{1/2}$ and the results at the long-wavelength edge approach Urbach's law. Deviations at low temperatures can be described by the influence of zero-point oscillations.

(5) Formulas derived from tight-binding exciton models describe the results obtained for the total integrated absorption and yield an oscillator strength of $f = 0.24$ as a lower limit for the transition.

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The author wishes to express his appreciation to Professor P. L. Hartman for his interest and encouragement, to Professor J. A. Krumhansl, Professor W. Martienssen, and Dr. T. Timusk for many valuable discussions, and to Mr. J. Ashe for growing the single crystals.

²⁰ D. L. Dexter, Phys. Rev. **101**, 48 (1956).

²¹ M. Lax and C. Herring, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenridge et al. (John Wiley & Sons, Inc., New York, 1956).

²² Z. Gyulai, Z. Physik **46**, 80 (1927).

²³ T. Ishii, J. Phys. Soc. Japan **16**, 1640 (1961).

²⁴ C. J. Rauch and C. V. Heer, Phys. Rev. **105**, 914 (1957).