

couples. Such an alloy might be more stable and reproducible than the present 2% Co alloy.

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### Ultraviolet Absorption of the Mixed System $\text{KCl-KBr}^\dagger$

HERBERT MAHR

*Laboratory of Atomic and Solid-State Physics, Cornell University, Ithaca, New York*

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The ultraviolet absorption of thin evaporated layers and the edge absorption of single crystals of the mixed system  $\text{KCl-KBr}$  were measured at room temperature in the photon energy range from 6–11 eV. In the thin layers, both the  $\text{Cl}^-$  and the  $\text{Br}^-$  absorption bands are present in the mixtures and their heights depend on the relative concentrations of the two ions. The energy values of the bands generally shift with composition, although in contrast to all the other bands, the high-energy  $\text{KBr}$  band shifts very little. The results obtained for the low-energy absorption bands can be described by a simple semiclassical electron transfer model. The behavior of the high-energy  $\text{KBr}$  band is discussed.

#### INTRODUCTION

PURE alkali halides are transparent throughout the visible into the ultraviolet range of the spectrum. There the absorption constant rises steeply to values above  $10^5 \text{ cm}^{-1}$ . As early as 1929, Hilsch and Pohl<sup>1</sup> found a series of rather sharp absorption maxima in this fundamental absorption region. They associated the first absorption band at the long-wavelength side with an electron transition from the halogen to the alkali ion. For the position of the absorption maximum, they gave the empirical formula

$$h\nu_{\text{max}} = \alpha(e^2/r) + E - I, \quad (1)$$

which fits the measurements within a few percent. Here  $\alpha=1.75$  is the Madelung constant for the  $\text{NaCl}$  structure,  $r$  the anion-cation distance,  $E$  the electron affinity of the halogen atom, and  $I$  the ionization energy of the alkali atom. Since then many investigators have extended the early measurements to higher photon energies and different temperature ranges. A recent comprehensive study by Eby, Dutton, and Teegarden<sup>2</sup> covered the absorption spectra of all alkali halides out to photon energies of more than 11 eV. Reflectivity measurements with single crystals by Hartman and co-workers<sup>3</sup> con-

firmed the results of the absorption measurements on thin evaporated layers.

Theoretical considerations concentrated on the first absorption maximum on the long-wavelength side, which was termed the exciton band.<sup>4</sup> Two models were proposed for the localized exciton in these ionic crystals. In one model the electron is transferred from the halogen ion to the nearest-neighbor alkali ions (electron-transfer model). The other model describes the exciton as an excited state of the halogen ion (excitation model). Attempts have also been made to classify the higher-energy absorption bands found experimentally in all alkali halides.<sup>5</sup>

Since it is difficult to correlate the various absorption bands in the different alkali halides, we have attempted to study the behavior of some particular bands under gradually varying conditions. For this reason, a system of mixed crystals of two alkali halides was used with the hope that it would provide more information about the nature of these absorption bands. Pick and Miessner<sup>6</sup> and Gnaedinger<sup>7</sup> used mixed crystals in a study of the  $F$  band and some  $V$  bands in the systems  $\text{KCl-KBr}$  and  $\text{KCl-RbCl}$ . Little information was obtained, however, on the influence of mixing in the fundamental absorption of the alkali halides. Hilsch and Pohl<sup>1</sup> measured an absorption maximum due to a 1% admixture of iodides to chlorides. For the case of the system  $\text{KI-CsI}$

<sup>†</sup> Work supported by the Office of Naval Research and the Advanced Research Projects Agency.

<sup>1</sup> R. Hilsch and R. W. Pohl, *Z. Physik* **57**, 145 (1929); **59**, 812 (1930).

<sup>2</sup> J. E. Eby, D. Dutton, and K. J. Teegarden, *Phys. Rev.* **116**, 1099 (1959).

<sup>3</sup> P. L. Hartman, J. R. Nelson, and J. G. Siegfried, *Phys. Rev.* **105**, 123 (1957).

<sup>4</sup> For a survey, see the review articles by: H. Haken, *Fortschr. Physik* **6**, 271 (1958) and T. Muto, *Progr. Theoret. Phys. (Kyoto) Suppl. No. 11*, 1 (1959).

<sup>5</sup> R. S. Knox and N. Inchauspé, *Phys. Rev.* **116**, 1093 (1959).

<sup>6</sup> H. Pick and G. Miessner, *Z. Physik* **134**, 576, 607 (1953).

<sup>7</sup> R. J. Gnaedinger, *J. Chem. Phys.* **21**, 323 (1953).

Martienssen<sup>8</sup> showed that the typical cesium-salt excitation bands disappeared. This effect was related to the change in lattice structure as the concentration of CsI was reduced.

In the present investigation the system KCl-KBr was used. It mixes completely in all compositions and its properties have been studied in detail by Wasastjerna<sup>9</sup> and co-workers. There is a small difference in lattice constants, and the exchange of the halogen, rather than the alkali, ions provides an undisturbed nearest-neighbor shell around each halogen ion.

#### EXPERIMENTAL TECHNIQUES

A vacuum ultraviolet monochromator with a gas discharge lamp (described elsewhere)<sup>10</sup> provided a useful light source from 5 eV to more than 12 eV. The transmission of thin evaporated layers was measured. LiF crystals were used as a substrate. Small pieces taken from KCl-KBr single crystals of known composition were evaporated. These single crystals were grown in a forming gas atmosphere and were later annealed. Small copper grids, coated with a thin carbon film by standard electron-microscope techniques, were placed next to the substrate. The lattice constant of the thin layers evaporated simultaneously on these grids was then determined with standard electron-diffraction techniques. The sharpness of the ring system obtained proved the uniform composition of the layers. It was assumed that the layers on the substrate have the same property. The composition of the layers was determined from the lattice constant using Kantola's<sup>9</sup> results. These compositions were the same as the concentrations in the melt from which the single crystals had been grown. In this way the lattice constant and composition could be checked for each run. The incident light intensity could be monitored by the external photoemission of CuI<sup>11</sup>; a screen of 3-mil wires coated with the CuI was placed in the incident beam. The transmitted light was measured by a photomultiplier coated with a sodium salicylate phosphor. It was found, using the CuI, that the intensity of the gas-discharge lamp was very stable over a period of several runs. Hence the actual transmission measurements were taken as the ratio of transmitted light before and after evaporation. A resolution of 2 Å was achieved with a low dark-current EMI photomultiplier. Both nitrogen and hydrogen gas were used in the discharge lamp. No correction for reflectivity was attempted, nor was the film thickness determined.

For some of the mixed salts, the absorption was also measured at liquid-nitrogen temperatures. This improved the resolution of the prominent absorption

bands, but the smaller maxima, which are resolved at liquid-nitrogen temperatures in the pure salts, were still not resolved in the mixtures.

#### EXPERIMENTAL RESULTS

In the first series of measurements, the absorption of thin layers of KCl-KBr mixed crystals was determined for various compositions at room temperature. Starting with pure KCl in Fig. 1 the result agrees with previous measurements.<sup>2</sup> For small additions of KBr, the prominent KCl absorption maxima still persist, although shifted in energy. In addition, new bands appear and grow with increasing KBr content. These bands finally develop into the prominent absorption maxima of pure KBr.<sup>2</sup> On the other hand, the KCl bands decrease and finally disappear in pure KBr. The Br<sup>-</sup> and the Cl<sup>-</sup> absorption bands are both present in the mixtures. The KCl I band and the second partner of the first KBr doublet, the KBr Ib band, overlap.

The dashed curves correspond to the maxima in the pure components. They have been scaled according to the concentration of the components, and their energies have been shifted so that the weighted sum of these dashed curves yields the measured spectrum. In each

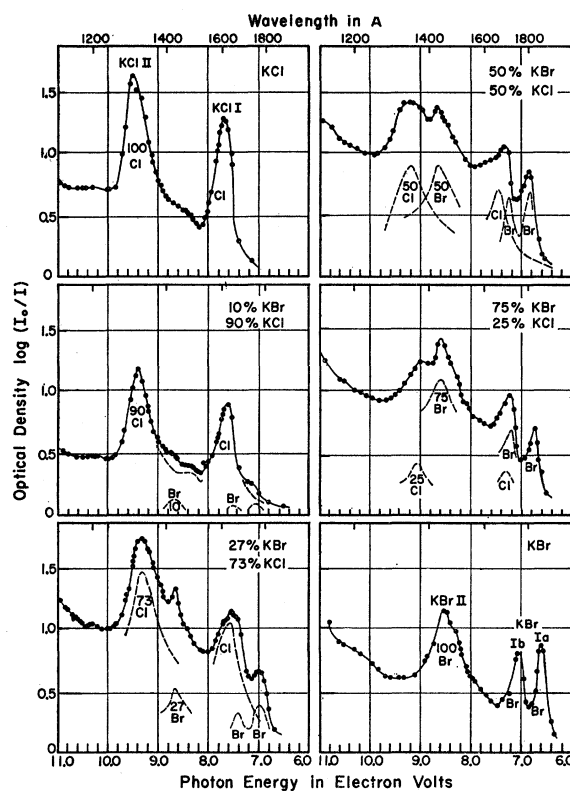


FIG. 1. The absorption spectra of thin evaporated layers of the mixed system KCl-KBr measured at room temperature. The compositions of the mixtures in mole percent are as indicated. The dashed curves represent the absorption maxima of the pure components. They are weighted according to their relative abundance and shifted in position.

<sup>8</sup> W. Martienssen, *J. Phys. Chem. Solids* **2**, 257 (1957).

<sup>9</sup> J. A. Wasastjerna, *Comment. Phys. Math.* **13**, No. 5, (1945-48); M. Kantola, *State Inst. Techn. Research, Finland No. 2* (1947).

<sup>10</sup> P. L. Hartman, *J. Opt. Soc. Am.* (to be published).

<sup>11</sup> G. Mattler, *Compt. rend.* **217**, 447 (1943).

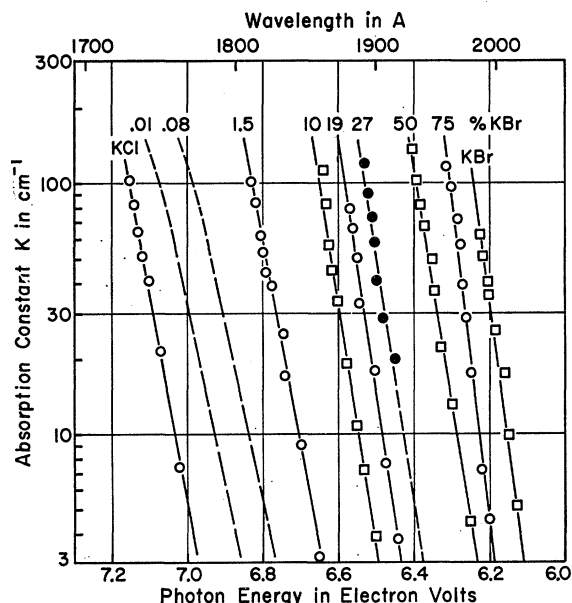


FIG. 2. The absorption constant  $K$  at the edge of the fundamental absorption (single crystals) measured at room temperature. The concentrations are given in mole percent. The two dashed lines are taken from measurements of Kobayashi and Tomiki.

case it was possible to synthesize the measured curve from the component peaks weighted according to concentration and shifted properly. (In this analysis, the approximate rather than the detailed shape of the absorption curve of the pure salt was used. A more precise analysis cannot be justified because the shape of the spectrum of the KBr component is not exactly equivalent to the shape for pure KBr. This is true because different absorption peaks shift by varying amounts in going from the pure crystal to a mixture).

In an attempt to study the long-wavelength edge of the first KBr exciton peak in these mixed crystals, thin cleaved single crystals were measured using the experimental techniques described above. The pure crystals were purchased from the Harshaw Chemical Company; the mixed crystals were grown from the melt from reagent-grade powder in a forming gas atmosphere and then annealed. Figure 2 shows the results. The absorption constant at the edge is plotted vs photon energy for various compositions. The result for pure KBr is in good agreement with Martienssen's<sup>8</sup> measurements. The edge shifts to higher photon energies with decreasing KBr concentration. The absolute value of the KBr exciton peak decreases, and in the limiting case the KCl edge is seen. For each of the compositions the absorption constant changes exponentially with photon energy, exactly as in the case of pure KBr (Urbach<sup>12</sup>—Martienssen<sup>8</sup> rule). For completeness, the two dashed curves are taken from results obtained by Kobayashi and

Tomiki.<sup>13</sup> These authors found an edge absorption due to small bromine impurities of the order of  $10^{-1}$  to  $10^{-3}\%$  KBr in purified KCl crystals. Their results fit nicely into the scheme of Fig. 2.

To show the shift of the absorption peaks for the thin layers, the energy positions of the prominent absorption maxima of Fig. 1 are plotted vs the molar concentration of KBr in Fig. 3. With increasing KBr content all the maxima shift to lower energies. The amount of change for the KBr II band is much less than for the other bands. The position of the edge of the fundamental absorption for mixed crystals is also plotted in Fig. 3. The value of  $K = 100 \text{ cm}^{-1}$  was chosen as representative for this edge. (The dashed line will be discussed in the next section.) The results of Kobayashi and Tomiki<sup>13</sup> can be used to extrapolate our measurements to very small bromine concentrations. These authors succeeded in evaluating the position of the KBr Ia peak in their dilute systems. This value has been indicated in Fig. 3 by the triangle. Our extrapolated value agrees with their result.

## DISCUSSION

The absorption spectra of both the  $\text{Cl}^-$  and  $\text{Br}^-$  ions can be identified in the evaporated layers of the mixed salts. The heights of the absorption peaks of the  $\text{Cl}^-$  and  $\text{Br}^-$  ions depend on the relative concentration of

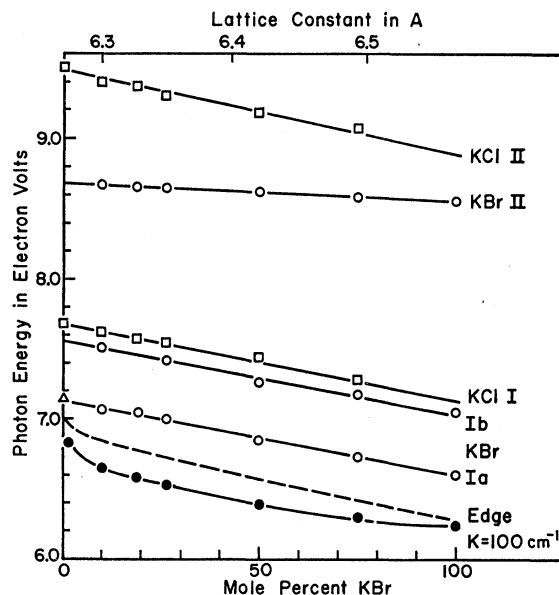


FIG. 3. The positions of the absorption maxima of the thin layers are plotted vs the concentration of KBr given in mole percent (open circles, Br bands; squares, Cl bands). The triangular symbol on the KBr Ia curve represents the position of this peak for very dilute systems, as measured by Kobayashi and Tomiki. The full circles are the measured energy positions of the edge absorption of single crystals for  $K = 100 \text{ cm}^{-1}$ . The dashed curve gives the calculated positions for the same absorption constant in ideal, undistorted mixtures.

<sup>12</sup> F. Urbach, Phys. Rev. **93**, 1324 (1953); F. Moser and F. Urbach, *ibid.* **102**, 1519 (1956).

<sup>13</sup> K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan **15**, 1350 (1960).

the two ions in the mixture. In addition, it has been found that all the prominent absorption maxima shift in energy with varying composition.

As a basis for the discussion of these results, we shall consider the electron-transfer model in its simplest semiclassical form. The photon energy necessary to transfer the electron from a halogen ion to a neighboring alkali ion is then given by

$$h\nu_{\max} = \alpha^*(e^2/r) + E - I - \text{polarization effects.} \quad (2)$$

In their empirical formula (1), Hilsch and Pohl<sup>1</sup> used  $\alpha^* = \alpha = 1.75$  which best fits the measured energy values of the absorption maxima of the pure salts. Their choice of  $\alpha^*$ , however, cannot be justified theoretically. Instead, the cycle process used to derive formula (2) leads to a value of  $(2\alpha - 1)e^2/r$  for the influence of the Coulomb lattice energy.<sup>14</sup> However, energy values for the first exciton peaks, calculated with  $\alpha^* = 2\alpha - 1 = 2.5$ , exceed by about 30% the measured values of the pure salts. Neither Hilsch and Pohl<sup>1</sup> nor Klemm<sup>14</sup> took polarization effects into account.

In the mixed system used here, each halogen ion is surrounded by 6 nearest-neighbor  $K^+$  ions throughout the mixtures. Only the next-nearest-neighbor halogen shell changes its composition. We shall now apply formula (2) to the low-energy absorption bands in KCl and KBr. In view of the above picture, we might assume that for a given absorption band only one parameter, the lattice constant, changes. Consequently, we conclude that the first term of formula (2) might explain the shift of the absorption maxima in Fig. 3. Therefore, in Fig. 4 we replot their positions vs the reciprocal of the lattice constant  $1/d$ . For all the bands, the measured peak energy changes proportionally to  $1/d$ .<sup>15</sup> From the slope of the straight lines of all the low-energy absorption bands, we calculate  $\alpha^* = 2.6$ . This shows that in a system where the significant change is the variation of the lattice constant, the model proposed by Klemm<sup>14</sup> gives a very good description of the experimental results.

A halogen site in the mixtures can be occupied either by a  $Cl^-$  or a  $Br^-$  ion, thereby giving rise to the two series of absorption bands observed in the mixtures. Figure 3 shows that the energy difference between the two first peaks of the  $Cl^-$  and  $Br^-$  series has the same value independent of the composition. Using formula (2) in the same way as Hilsch and Pohl<sup>1</sup> we conclude that this difference is a result of the different electron affinities of the  $Cl^-$  and  $Br^-$  ions. The difference in electron affinities given in the literature<sup>16</sup> (0.21–0.34 eV) is smaller than the energy difference of 0.53 eV derived from Fig. 3.

<sup>14</sup> W. Klemm, Z. Physik **82**, 529 (1933).

<sup>15</sup> As the relative changes of the lattice constant are small over the range of mixtures, a plot against the lattice constant yields as good a straight line as a plot against the reciprocal of the lattice constant.

<sup>16</sup> H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie* (Springer-Verlag, Berlin, 1950), Vol. 1, Part 1, p. 213.

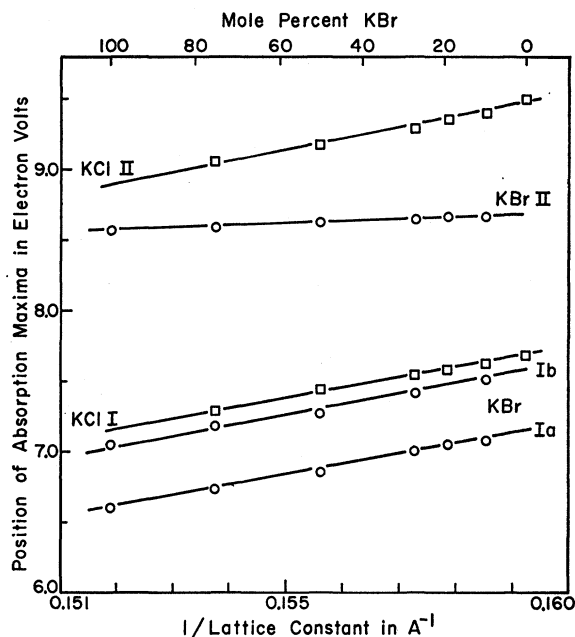


Fig. 4. The energy positions of the prominent absorption maxima of the thin layers are plotted vs the reciprocal of the lattice constant of the mixtures (open circles, Br bands; squares, Cl bands).

For the low-energy absorption bands the predictions of a simple electron-transfer model give a very useful description of our results. Both the influence of the electron affinity of the central halogen ion and the importance of the Coulomb lattice energy can be seen in our results. The doublet splitting of the first KBr band, which can be accounted for by the electron transfer model, can also be seen in the mixed crystals. The amount of splitting is found to be independent of composition, as one would expect.

The higher-energy absorption band in KBr behaves differently. It is almost independent of composition or variations of the lattice constant. Two possibilities exist to account for this difference in behavior. We could describe both high energy bands, the KCl II and the KBr II band, as bound exciton states. The KCl II band would correspond to an electron transfer from the central  $Cl^-$  ion to an excited state of the potassium atom. This description was used by Hilsch and Pohl<sup>1</sup> in their early paper. The fact that the KBr II band does not change with the lattice constant leads us to the assumption that an excitation at one particular ion site gives rise to the absorption peak. The excited level of the  $Br^-$  ions is, however, far too low and the excited level of the  $K^+$  ion far too high to account for the experimental value of 8.6 eV for this transition. If a transfer model which considers transfer to bound states with larger radii were assumed, rather special assumptions would be necessary to explain this invariance of the KBr II band.

A different possibility would be to correlate the high-

energy absorption bands with transitions from the valence band to the conduction band. We can use the fact that these absorption bands in both KCl and KBr are beyond the step found in the absorption curves of the pure salts. This step was generally<sup>3,17</sup> taken as the onset of band to band transitions. The shape of the two absorption maxima, KCl II and KBr II, would then reflect the structure of the density of states in the valence and conduction bands. It is known that both bands are quite independent of temperature variations, in striking contrast to the strong temperature dependence of the lower bands. In this case then, the similarity of the KCl II band shift with that of the lower bands is only coincidental. We would have to assume in our energy-band picture that, as the total number of states decreases with decreasing concentration of a component, the distribution of the density of states remains the same. Only direct evidence of the existence of free electrons would enable us to decide in favor of an energy-band structure model rather than a bound-state model.

We shall now discuss the broadening of the absorption bands resulting from the mixing of two ions of different sizes. We shall deal with the KBr Ia peak only, because the measured edge absorption of this peak should be very sensitive to changes of the bandwidth in the mixtures. As seen from Fig. 2, the edge absorption varies exponentially with the photon energy. We can therefore use Martienssen's<sup>8</sup> results for the edge absorption of pure KBr and calculate the position of the absorption constant  $K=100\text{ cm}^{-1}$  in the mixtures under the following assumptions: (1) The bandwidth does not change in the mixtures, and (2) The absolute height of the absorption maximum decreases in proportion to the decrease in KBr content. The result is given by the dashed line in Fig. 3. The measured energy positions for the same absorption constant are off by 50% in some of the mixtures. We interpret this deviation as caused by a lattice distortion due to the mixing of KCl and KBr. This description is strengthened by observations of Wasastjerna and co-workers.<sup>9</sup> Using x-ray diffraction methods they found an increase in the mean-square displacement of the  $\text{K}^+$  ions in a 50:50 mixture of

KCl-KBr over that measured in the pure crystals. They interpreted this increase as due to a lattice distortion.

### CONCLUSIONS

(1) The absorption spectra of both the  $\text{Cl}^-$  and the  $\text{Br}^-$  ions can be identified in the thin layers of the mixed salts. The heights of the absorption maxima of the  $\text{Cl}^-$  and the  $\text{Br}^-$  ions depend on the relative concentrations of the two ions in the mixture.

(2) The energy values of the bands shift downward with increasing KBr content. In contrast to all the other bands, the higher energy KBr II peak shifts very little.

(3) The predictions of a simple semiclassical electron-transfer model are in close agreement with the results obtained for the low-energy absorption bands. The influence of the electron affinity of the halogen ions and the importance of the Coulomb lattice energy are both found in the results.

(4) The invariance of the high-energy KBr II absorption peak with lattice constant might be caused by electron transitions into bound exciton states of a more specialized nature, such as excited levels of particular ions or exciton orbits of larger radii. It is more likely that both high-energy absorption peaks in KCl and KBr arise from transitions into the conduction band, and their shapes reflect the energy-state distribution of valence and conduction band.

(5) In mixed single crystals the absorption at the long-wavelength edge of the first KBr peak varies exponentially with photon energy as found previously in pure KBr crystals. The edge, however, shifts to higher energies with decreasing KBr content. A broadening of this absorption tail in the mixtures can be described in terms of a lattice distortion.

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<sup>17</sup> E. H. Taft and H. R. Philipp, *J. Phys. Chem. Solids* **3**, 1 (1957).