AN ABSTRACT OF THE THESIS OF

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(Name) (Degree) (Major)

Date thesis is presented January 4, 1963

Title INTERACTIONS OF SULFATE IONS IN POTASSIUM CHLORIDE CRYSTALS

Approved
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Single crystals of potassium chloride doped with potassium sulfate were grown in a nitrogen atmosphere using the Kyropoulos technique. Radioautograms were made of crystals grown from melts containing radioactive sulfur as potassium sulfate. These indicated that melt stirring by crystal rotation at 90 rpm was sufficient to reduce random variations in potassium sulfate concentration to about 1 percent. The distribution coefficient for potassium sulfate (crystal concentration/melt concentration) was determined by radiotracer dilution analysis to be $1.0 \times 10^{-3}$.

The infrared spectra of the crystals indicated colloidal precipitation of the potassium sulfate. The crystals remained optically clear, however, with sulfate ion concentrations up to about $5 \times 10^{16}$ cm$^{-3}$.

Divalent metal sulfates (those of magnesium, calcium, barium and lead) were found to dissolve in potassium chloride to form
isolated $\text{MSO}_4^-$ ion pairs. The sulfate ion in an $\text{MSO}_4^-$ ion pair is substituted for a chloride ion with each oxygen atom directed toward the corner of the unit cell containing the sulfate ion, and the divalent metal ion is substituted for one of the nearest neighbor potassium ions. The asymmetric stretching band of the sulfate ion in potassium chloride, denoted the alpha band, was observed at $1135 \text{ cm}^{-1}$. In an $\text{MSO}_4^-$ ion pair the symmetric stretch of the sulfate ion has been rendered slightly active, and the degeneracy of the asymmetric stretch has been removed. The peak positions for the case of $\text{CaSO}_4$ are $\beta_1$ (symmetric mode) = $982 \text{ cm}^{-1}$, $\beta_2 = 1090 \text{ cm}^{-1}$, $\beta_3 = 1157 \text{ cm}^{-1}$ and $\beta_4 = 1185.5 \text{ cm}^{-1}$.

A perturbation calculation of the splittings was carried out, and, except where covalency was a factor, the calculated values for the unperturbed asymmetric stretching frequency agreed well with the observed position of the alpha band. The unperturbed frequency of the symmetric stretch was found to be $992 \text{ cm}^{-1}$, and the force constant of the sulfur-oxygen bond was calculated to be $7.79$ mdyne/A neglecting coupling with the bending modes.

When crystals doped with potassium sulfate were additively colored, decomposition of the sulfate ion occurred. The infrared spectra of the colored crystals showed no absorption in the asymmetric stretching region of the sulfate ion, but did show an
absorption at 875 cm$^{-1}$ which is attributed to either SO$_2^-$ or SO$_2^2$. The reduction products of the sulfate ion were observed to enhance the rate of bleaching of the F band with F light, to inhibit formation of the R bands, and to give rise to several new absorption bands. A band called the $S_1$ band at 284 mµ is felt to arise by promotion of an electron from a divalent anion to an associated negative ion vacancy. A band at 364 mµ may arise from the $F^+_{2}$ center.

A short study of the behavior of the N bands in pure potassium chloride and a survey of recent literature led to postulation of linear aggregates of three and four F centers as the centers giving rise to the $N_1$ band. Models for the $N_2$ centers are discussed, as well as mechanisms for color center reactions.
INTERACTIONS OF SULFATE IONS IN POTASSIUM CHLORIDE CRYSTALS

by

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A THESIS submitted to OREGON STATE UNIVERSITY

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

June 1963
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Date thesis is presented  January 4, 1963

Typed by Carol Baker
ACKNOWLEDGMENTS

The author is indebted to Dr. Allen B. Scott for his many helpful suggestions and criticisms, and to the Office of Naval Research for its support of the project. The help of Dr. J.C. Decius in interpreting the infrared spectra as well as in performing the perturbation calculation is gratefully acknowledged. Others to whom thanks is due include Paul M. Gruzensky, who grew one of the crystals used in the study; Robert E. Woodley, who measured the intensity of the spectrophotometer light source; and Miss Sandra Buxton, who assisted with part of the radioactive analyses. Finally, the author wishes to express his deepest appreciation to his wife Marjory, who made the drawings and assisted greatly in the preparation of the manuscript, cheerfully accepting the many demands which this work has placed upon her.
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INTERACTIONS OF SULFATE IONS IN POTASSIUM CHLORIDE CRYSTALS

INTRODUCTION

The beauty and apparent perfection of well-formed single crystals have long fascinated mankind. A few have achieved commercial importance because of their rarity and durability, and others because of their optical or electrical properties. While the geometrical form of single crystals suggested orderly arrangement at the atomic level, it was not until Laue's discovery of the diffraction of x rays by crystals in 1912 that determination of crystal structure first became possible.

When Planck postulated his light quanta to account for the frequency distribution of light emitted from a black body, Einstein was quick to see that a similar postulate could qualitatively account for the specific heats of solids. Thermal properties and the behavior of intrinsic semiconductors proved to be quite susceptible to quantum-mechanical explanation. It soon became evident, however, that properties such as plasticity and electrolytic conductivity of crystals could not be explained on this basis alone. These properties found their explanation in crystalline imperfections.

Linear imperfections were first postulated to account for the plasticity of metals (1, p. 103), but these also exist in ionic crystals, and are responsible for their plastic behavior. The Taylor-Orowan
or edge dislocation exists in crystals as a result of incomplete formation of atomic planes. While a void will exist at the terminus of an incomplete plane, it does not extend to the boundary of the crystal because the adjacent atomic planes are curved toward each other. The lattice rapidly approaches periodicity with increasing distance from the dislocation.

The second general type of dislocation is the Burger or screw dislocation. It is characterized by the fact that one can pass continuously from one crystallographic plane normal to the dislocation to the next such plane by passing around the dislocation, more or less as if one were proceeding up a spiral staircase. The screw dislocation is important in the theory of crystal growth (21; 80, p. 28-30). Both edge and screw dislocations have been observed by electron microscopes of very high resolving power (1, p. 104; 68).

Diffusion, and in ionic crystals, the closely related phenomenon of ionic conductivity, are dependent on the existence of point defects. In pure crystals these may be of two general types: unoccupied lattice sites, and atoms or ions in other than normal lattice positions. Since the point defects in ionic crystals may bear an effective charge, the concentration of defects of each sign is such that electroneutrality is preserved. In silver chloride, interstitial silver ions and silver ion vacancies are the important point defects (42, p. 295), while in alkali
halides the positive and negative ion vacancies are the important species (53, p. 499; 54).

Another type of point defect is that introduced by a trace impurity. Of particular importance are those impurities whose charge or number of valence electrons is different from that of the ion or atom replaced in the host lattice. Elements of groups III and V introduce holes and free electrons into crystals of silicon and germanium. If an alkali metal ion in an alkali halide crystal is replaced by an alkali metal atom, the atom is unstable with respect to loss of the single outer s electron to the conduction band, and the electron moves through the conduction band until it is trapped at some imperfection. The negative ion vacancy is an effective trap for an electron at room temperature. An electron trapped at such a vacancy absorbs visible light, and so imparts color to the crystal. Hence it is called a color center, and specifically an F center, from the German "farbzentrum." Light absorption at room temperature by the F center in alkali halides leads to the formation of more complex color centers (62). The models of some of these color centers are current literature topics.

If a divalent cation is introduced into an alkali halide crystal at the site of an alkali metal ion, it is necessary to introduce a positive ion vacancy as well to preserve electroneutrality. Both of these point defects affect the properties of the crystal. The divalent cation
introduces additional electronic energy levels into the crystal, and
may therefore trap electrons optically promoted from an F center
(61, p. 81-82). In potassium chloride, the ionic conductivity is pro-
portional to the number of positive ion vacancies, and so is enhanced
by doping with a divalent metal chloride (39, p. 706).

Introduction of sulfate ion into potassium chloride was first
undertaken because of possible effects on color center behavior. It
was thought that the sulfate ion might introduce free negative ion va-
cancies into the crystal. An increase in the concentration of negative
ion vacancies would increase the probability that an electron optically
promoted from an F center would be trapped again in a negative ion
vacancy. This would reduce the rate of formation of complex centers.
In contrast to expectations, irradiation of the colored crystals with F
light led to a more rapid decrease in the F band than that which occurred in crystals not doped with potassium sulfate.

Since the sulfate ion is polyatomic, it absorbs in the infrared
region of the spectrum. It was hoped that the oscillator strength of
the triply degenerate stretching mode near 1100 cm$^{-1}$ could be deter-
mined, and that this would eliminate the need for more tedious
analysis of the crystal by other methods. The first crystals grown
proved to have not only one, but several absorption bands in this re-
gion, indicating that the degeneracy was being removed by
electrostatic asymmetries in the environment of the sulfate ion.

Elucidation of the spectra of crystals of potassium chloride containing potassium sulfate proved to be one of the most significant aspects of this work.

The ionic conductivity of potassium chloride crystals containing potassium sulfate has been investigated by Gruzensky (23), and the photoconductivity of the crystals following additive coloration has been studied by Hardtke (25). Both investigations were carried out in this laboratory.
INCORPORATION OF SULFATE ION IN POTASSIUM CHLORIDE SINGLE CRYSTALS

Experimental

Reagents

The potassium chloride used in growing most crystals was reagent grade, doubly recrystallized. Two crops were taken in the second recrystallization after discarding a small first crop. Potassium sulfate used for doping the crystals was also doubly recrystallized reagent grade.

Crystal-Growing Apparatus

Potassium chloride single crystals were grown from the melt using the Kyropoulos technique (43). An apparatus was constructed for growth of uniformly doped crystals in a controlled atmosphere. The apparatus, in which growth of a rotating seed crystal proceeds as the level of the molten salt is lowered, is illustrated in Figures 1 and 2. While the platinum crucible containing the melt was lowered on a base plate at 4.8 cm/hr, the growth rate was about 20 percent greater than this due to depletion of the liquid in the crucible by the growing crystal. The rotation rate of the seed crystal could be varied continuously from 30-200 rpm.

The furnace was made by wrapping nichrome wire on an
Fig. 1. - The crystal-growing apparatus
Fig. 2. - Schematic diagram of the crystal-growing apparatus
alundum core, and covering the windings with alundum cement. Asbestos flour was used for insulation. The water jacket surrounding the furnace was constructed of brass and the base plate was of steel; both were nickel plated. The rotating rod to which the seed crystal was attached was made of stainless steel. A Pyrex bell jar was used.

**Growth Procedures**

After placing 35-40 g of salt in the platinum crucible, the bell jar was put into place and was evacuated overnight with the salt slightly warmed. A typical pressure of about 50μ resulted. Liquid-pumped nitrogen was then introduced into the system. The nitrogen was freed of oxygen by passing the gas over hot copper filings, and water vapor was removed by passing through a liquid nitrogen trap. A second evacuation to a pressure of about 10 mm, followed by another backfilling with the purified nitrogen, gave an inert atmosphere having maximum impurities of a few ppm. Most of the impurity in the nitrogen consisted of water vapor from slight leaks in the furnace water jacket. Crystals were grown at a nitrogen pressure of a few mm in excess of atmospheric.

The salt was melted prior to backfilling to minimize sublimation of the potassium chloride. Sublimation was appreciable when the atmosphere was sufficiently dense to support the sublimed salt, and
was most severe before crystal growth was started.

The furnace current was regulated so that the tip of the seed crystal was melted on contact with the molten salt; this was done to insure the formation of a single crystal. Continued contact between the melt and the seed crystal was confirmed by reflection of light from the melt surface, which curved upward at the edges of the seed crystal. Rotation of the seed crystal and lowering of the melt were begun, and the furnace current was lowered in small increments until the crystal had grown to the proper cross section. Only slight adjustments were required for the duration of crystal growth. When the greater part of the melt had been crystallized, contact with the melt was broken and the system was allowed to cool to room temperature. The crystals were typically 1.2-1.4 cm square in cross section and 2-3 cm long.

Uniformity of Potassium Sulfate Concentration

Importance of Stirring

Potassium sulfate is more soluble in the melt than in the crystal. As the growing crystal rejects the sulfate ion, the concentration of the ion in the melt is built up at the interface. The effective distribution coefficient is dependent upon the sulfate ion concentration at the interface, which in turn depends upon the growth rate, the
amount of melt agitation or stirring and the diffusion coefficient of the sulfate ion. This effect has been studied both theoretically and experimentally by Burton (7, 8). Stirring is conveniently accomplished by rotation of the crystal; this must be rapid enough so that rotational stirring predominates over random stirring by convection currents.

**Rate of Rotation Required for Uniformity**

The degree of uniformity of sulfate ion concentration in the crystals was studied by means of a radiotracer technique. Addition of about 1 mc of $^{35}\text{SO}_4^-$ to the potassium sulfate used in doping gave crystals with sufficient activity above the $^{40}\text{K}$ level for the production of radioautograms. $^{35}\text{S}$ decays by beta emission to the inactive $^{35}\text{Cl}$, and has a half-life of 87.1 days. The maximum energy of the beta radiation is 0.167 Mev.

A base tracer solution of about 0.2 mc/ml was prepared by dilution of carrier-free $^{35}\text{S}$ as sulfuric acid, obtained from Oak Ridge National Laboratory. Enough potassium sulfate was added to make the $\text{K}_2\text{SO}_4$ concentration of the solution of 0.1 mg/ml. From this base solution 50 µl was withdrawn and diluted to one liter, the potassium sulfate concentration being raised again to 0.1 mg/ml.

To dope the melt with radioactive sulfate, 5 ml of the base
tracer solution was transferred to the empty platinum crucible and dried under a heat lamp. An additional amount of potassium sulfate, as well as potassium chloride, was then added to the crucible; growth of the crystal proceeded in the usual manner. Care was taken to minimize contamination of the apparatus by the radioactive material. After growth of the crystal, the area was examined with a survey meter. Contamination was removed from the bell jar and other surfaces by washing.

Crystals containing $^{35}$S were grown at different rates of rotation of the seed crystal. Cuts were made parallel to the growth axis of the crystal as well as cuts perpendicular to it; the cleaved surfaces of the crystal portions obtained were placed next to x-ray film in the dark and an exposure of several days was allowed before developing the film.

Three examples of radioautograms, taken of crystals grown at different rotation rates and cleaved parallel to the growth axis, are shown in Figure 3 (a)-(c). Dark portions of the radioautogram are due to $^{35}$S activity, and insufficient rotational stirring is indicated by a dark line near the edge of the crystal. A rotation rate of 90 rpm is seen to be sufficient to give crystals which are uniform except for the predictable increase of sulfate ion concentration along the axis of growth, due to the increasing concentration of the melt during growth of the crystal. A densitometer trace of the radioautogram of the
Radioautograms are shown of KCl(K₂SO₄) crystals containing ^35S, grown at rotation rates of (a) 0 rpm (b) 30 rpm and (c) 90 rpm and cleaved parallel to the growth axis. Dark portions indicate ^35S activity.

Radioautograms are shown of crystals grown at rotation rates of (d) 30 rpm and (e) 85 rpm and cleaved perpendicular to the growth axis.

Fig. 3. - The effect of stirring by crystal rotation upon distribution of K₂SO₄ in KCl crystals
crystal grown at 90 rpm was taken on a Photovolt Electronic densitometer, model 525, using a circular aperture of about 2 mm diameter. The trace showed a uniform increase in density along the growth axis, with fluctuations not exceeding about 2 percent.

Sulfate Ion Distribution in Crystals Grown with Insufficient Stirring

A rather interesting effect is noted in crystals not rotated rapidly enough to give uniform sulfate ion concentration, as shown in Figure 3 (d), (e). Radioautograms of crystals cleaved perpendicular to the growth axis show a circular center portion of uniform potassium sulfate concentration, separated from an outer region of lower concentration by a narrow ring of considerably higher concentration. This narrow ring appears as a line in crystals cut parallel to the growth axis. It moves outward with increased rotation rate so that in the radioautogram of the crystal grown at 85 rpm it is only faintly visible at the corners of the crystal.

The effect appears to be associated with the shape of the interface between the crystal and the melt. Without rotation, the bottom surface of the crystal is convex as the melt is heated only at the sides. The effect of rotation is to draw the melt down the sides of the crucible and then up toward the crystal. The center of the interface at intermediate rotation rates was noted to be slightly concave with
respect to the crystal, suggesting that in this case the center of the melt is the hottest, having been freshly drawn from the heated sides, and that the melt cools as it flows outward along the interface. As the rate of rotation is increased, thermal gradients are finally reduced to such an extent that the interface is flat except for a slight upward curve at the edges of the crystal. These effects are illustrated in the following diagram, which shows the approximate shape of the bottom surface of the crystal at various rotation rates.

\[
\begin{array}{ccc}
0 \text{ rpm} & 45 \text{ rpm} & 90 \text{ rpm} \\
\end{array}
\]

In crystals grown with insufficient stirring, the area of lowest sulfate ion concentration is associated with the convex outer portion of the crystal, the inner area of uniform concentration with the slightly concave portion, and the ring of highest concentration with the part of the crystal extending farthest into the melt.

The rate limiting process in precipitation of ions on the crystal may be either the precipitation of the ions or the formation of stable precipitation sites. The latter may consist of lattice imperfections, such as screw dislocations, or ions foreign to the crystal (80, p.149). An ion which precipitates on a plane surface has only one point of contact with the crystal, and with the usual degree of supersaturation or
supercooling, it is most probable that the ion will leave the site before an ion of opposite sign is precipitated next to it. The starting of new planes is enhanced by some impurities, generally those which complex with one or the other of the ions of the crystal. Lead ion, for example, complexes with the chloride ion. This complex is less likely to be dislodged when it precipitates, because of its high molecular weight. The sulfate ion, due to its double charge, is more tightly bound to potassium ions than is the chloride ion, and may be considered to have formed a loose complex. The greatest amount of new plane formation occurs in the region of the interface extending farthest into the melt, and the least amount occurs at the convex edges of the crystal; the slightly concave inner portion of the interface is intermediate. It is apparent from the radioautograms that the sulfate ion is involved in the formation of new planes.

Precipitation Patterns of Excess Doping Agent

When the doping agent in the melt became too concentrated, it began to precipitate as a second phase on the growing crystal. Photographs of some patterns shown by calcium sulfate in potassium chloride crystals cleaved perpendicular to the growth axis are shown in Figure 4. Generally, a square whose diagonals are perpendicular to the edges of the crystal may be observed. The square is sometimes
Fig. 4. - Precipitation patterns of CaSO$_4$ in KCl
(Crystal cross-sections enlarged about 2x)
filled in only partially; the diagonals may be prominent. It is felt that this phenomenon must be associated with the formation of strands or one-dimensional crystals of calcium sulfate.

The Distribution of Sulfate Ion between Melt and Crystal. The concentration of sulfate ion in the potassium chloride crystal which was grown at 90 rpm and shown to be uniform by a radioautogram was determined by tracer dilution analysis. The top and bottom of the crystal were cleaved away, leaving a uniform bole. This bole was cut perpendicular to the growth axis into four pieces. From each of these pieces a smaller portion was obtained for analysis, by cleaving parallel to the growth axis. The smaller portions had only cleaved surfaces, the original crystal surface having been cut away.

Standards for the analysis were prepared as follows: Three ml of the diluted \(^{35}\)S tracer solution, whose preparation was described earlier (p. 11), was combined with 560 mg \(K_2SO_4\), 800 mg \(BaCl_2\cdot 2H_2O\), 0.5 ml concentrated HCl, and sufficient water to give about 40 ml total volume. After digesting for about two hours, portions of the barium sulfate precipitate were deposited in steel cup planchets and dried under a heat lamp. The planchets were of infinite thickness as confirmed by weighing.

Similarly, four additional sets of three planchets each were prepared using identical amounts of reagents except that for each set one
of the smaller pieces of the crystal was substituted for the 3 ml of diluted tracer solution. All planchets were counted using a gas-flow Geiger-Muller counter with a thin window of Mylar plastic, and count rates were corrected for background.

The average concentration, \( \overline{C}_c \) (expressed as weight of \( K_2SO_4 \) per weight KCl) of potassium sulfate in the crystal portions was calculated from the equation

\[
\overline{C}_c = \frac{V_s}{V_d} \cdot \frac{A_c}{A_s} \cdot \frac{W_d}{W_c}
\]

where \( V_s \) is the volume of base tracer solution in the standard aliquot and \( V_d \) the volume of base tracer solution used to activate the crystal, \( A_c \) is the average activity of the three planchets made from a given piece of crystal and \( A_s \) the average activity of the standard planchets, and \( W_d \) is the weight of the potassium sulfate used in growing the crystal, \( W_c \) being the weight of the crystal portion under analysis.

Assuming that the amount of potassium sulfate incorporated in the crystal is negligible with respect to that left in the melt, the distribution coefficient for sulfate ion between melt and crystal phases of potassium chloride may be calculated from the formula

\[
K = \frac{C_c}{C_m} = \frac{-M_c}{M} \frac{\overline{C}_c}{W_d \ln \left(1 - \frac{C_c}{M_1} \right)}
\]
where $C_c$ is the concentration of potassium sulfate in the crystal, $C_m$ is that in the melt, $M_c$ is the weight of one of the four crystal pieces from which a smaller piece of weight $W_c$ was cut for analysis, and $M_i$ is the weight of melt remaining before the portion weighing $M_c$ began to crystallize. In this case $W_d$ was equal to $83.6 \times 10^{-3}$ g.

The concentration of potassium sulfate in the four crystal portions, and the distribution coefficient calculated for each portion, are given in the following table.

Table 1. Calculation of the distribution coefficient for sulfate ion between melt and crystal phases of potassium chloride

<table>
<thead>
<tr>
<th>Crystal sample #</th>
<th>$M_i$, g</th>
<th>$M_c$, g</th>
<th>$C_c$</th>
<th>$K_{2SO_4}/g$ KCl</th>
<th>$10^3 K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.7</td>
<td>2.66</td>
<td>2.32</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>35.0</td>
<td>2.49</td>
<td>2.64</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>32.5</td>
<td>2.77</td>
<td>2.82</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>29.8</td>
<td>1.61</td>
<td>2.97</td>
<td>1.03</td>
<td></td>
</tr>
</tbody>
</table>

The average value of the distribution coefficient was found to be $1.04 \times 10^{-3}$. It must be emphasized that this is an effective distribution coefficient depending on the growth and rotation rates, and is higher than the equilibrium distribution coefficient.
Theoretical

Modes of Incorporation of the Sulfate Ion in Potassium Chloride

Lattice Geometrical Considerations

There are many conceivable modes of incorporation for the sulfite ion in potassium chloride. It might be incorporated interstitially, or be substituted for the chloride ion. Because of its size it might be incorporated in lieu of several chloride and potassium ions; that is, it could be situated within a vacancy aggregate.

In order to determine the structure of the important point defect or defects in the crystal which involve the sulfite ion, different possible modes of incorporation were investigated for total strain in the hard-sphere approximation. Strain is defined here as the distance which ions overlapping with the sulfite ion in a rigid lattice must be moved to eliminate the overlap.

Ionic and Atomic Radii. The Pauling radii of the chloride and potassium ions are 1.81 A and 1.33 A, respectively. The sulfur-oxygen distance in the sulfite ion is nearly constant for alkali metal sulfates, having a value of 1.51 A. To obtain a suitable oxygen radius, the nearest metal-oxygen distances for several sulfates of the alkali metals and alkaline-earth metals were tabulated from the
literature and the Pauling radius of the metal ion was subtracted from the M-O distance, as shown in the following table.

Table 2. Calculation of the radius of oxygen in the sulfate ion

<table>
<thead>
<tr>
<th>Metal</th>
<th>M-O distance, Å</th>
<th>Pauling radius of metal ion, Å</th>
<th>Radius of oxygen, Å</th>
<th>Reference for M-O distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>3.10</td>
<td>1.69</td>
<td>1.41</td>
<td>(56, p. 362)</td>
</tr>
<tr>
<td>Rb</td>
<td>2.89</td>
<td>1.48</td>
<td>1.41</td>
<td>(56, p. 362)</td>
</tr>
<tr>
<td>K</td>
<td>2.71</td>
<td>1.33</td>
<td>1.38</td>
<td>(56, p. 362)</td>
</tr>
<tr>
<td>Na</td>
<td>2.31*</td>
<td>0.95</td>
<td>1.36</td>
<td>(81)</td>
</tr>
<tr>
<td>Na</td>
<td>2.29</td>
<td>0.95</td>
<td>1.34</td>
<td>(73, p. 189)</td>
</tr>
<tr>
<td>Mg</td>
<td>2.01</td>
<td>0.65</td>
<td>1.36</td>
<td>(64)</td>
</tr>
<tr>
<td>Ca</td>
<td>2.34</td>
<td>0.97</td>
<td>1.37</td>
<td>(74, p. 286)</td>
</tr>
</tbody>
</table>

*A different crystal structures

A value of 1.36 was used in strain calculations as the radius of oxygen in the sulfate ion.

Interstitial Incorporation

For the sake of completeness, interstitial incorporation of the sulfate ion in potassium chloride was considered. The four centers found to have the lowest total strain will be discussed.

Body-Centered Interstitial Centers. One interstitial center
is that in which the sulfate ion is within an elementary cube, as shown schematically in Figure 5. One of the four oxygen atoms is directed toward one of the corner chloride ions, and the other three rest against the opposite potassium ion. When equal strain is assumed for the \( K^+ \) and \( Cl^- \) ions on the threefold axis of the center, the three \( O \) atoms not on the axis are nearly in the \( (111) \) plane of the \( Cl^- \) ions which are adjacent to the \( K^+ \) ion on the axis. Because of this, the most favorable orientation is that in which the three \( O \) atoms rest between the three \( Cl^- \) ions. In other words, the angle between the \( Cl^- \) ions and the three \( O \) atoms on a projection along the threefold axis is 60°. A second center is that in which the positions of the potassium and chloride ions are reversed. The individual and total strains are given for both cases in the figure.

**Face-Centered Interstitial Centers.** In the third interstitial center, shown in Figure 6, the sulfate ion penetrates a face center of the simple cube. Two oxygen atoms are located within each of two adjacent simple cubes. The fourth center is the enantiomorph of the third, and is produced by reflection through the plane of the face common to the two simple cubes.

**Simple Substitutional Incorporation**

Two modes of substitution of the sulfate ion for the chloride ion
Fig. 5. - Sulfate ion in KCl: Body-centered interstitial centers

The sulfur atom and one of the oxygen atoms of the sulfate ion are located on the simple cube diagonal (axis of threefold symmetry) and the remaining oxygen atoms are rotated to a position of minimum strain. In the center illustrated, three K⁺ ions are each strained by 0.57 Å, one K⁺ by 1.07 Å, three Cl⁻ by 0.80 Å, and one Cl⁻ by 1.07 Å, for a total strain of 6.3 Å. Another center results when the positions of the K⁺ and Cl⁻ ions are reversed. In this case, the strains are: three K⁺ by 0.28 Å, one K⁺ by 1.02 Å, one Cl⁻ by 1.02 Å, and three Cl⁻ by 1.08 Å, for a total of 6.2 Å.
Fig. 6. - Sulfate ion in KCl: Face-centered interstitial centers

The sulfate ion penetrates a face center of the simple cube. For the center illustrated and its non-superimposable mirror image, the strains are: two K$^+$ ions, each by 1.04 Å, four Cl$^-$ by 0.39 Å, and two Cl$^-$ by 1.57 for a total of 6.8 Å.
are probable. One is the symmetrical substitution in which each oxygen atom is directed along a diagonal of the unit cell (Figure 7). Each of the nearest-neighbor potassium ions is strained outward slightly. The second substitutional mode, shown in Figure 8, is called the unsymmetrical mode even though it has two planes of symmetry.

Incorporation within Vacancy Aggregates

Symmetrical Neutral Center. If the two chloride ions which are common to the two simple cubes in the face-centered interstitial center are removed, a center is obtained in which the sulfate ion is in a saddle position between two Cl\(^-\) ion vacancies. Because of its relatively high symmetry and effective charge, this center (not illustrated) is called the symmetrical neutral center. The two potassium ions in the cube face from which the chloride ions were removed are each strained by 1.04 A, while the four Cl\(^-\) ions on the opposing faces of the two simple cubes are each strained 0.39 A, for a total strain of 3.64 A.

\(C_{2v}\) Negative Center. Removal of one of the two potassium ions which are strained in the symmetrical neutral center results in a center with an effective negative charge. Since the positive and two negative ion vacancies form a complex with \(C_{2v}\) symmetry, the
Fig. 7. - Sulfate ion in KCl: Symmetrical substitutional center

The sulfate ion is substituted for a chloride ion in a highly symmetrical arrangement, each oxygen atom being directed along a diagonal (dotted line) of the unit cell. Six $K^+$ ions are strained outward 0.12 Å each for a total strain of 0.72 Å.
The sulfate ion is substituted for a chloride ion, with two of the oxygen atoms located on a (dotted) line passing through the cube center and two of its next-nearest neighbors. Although this center has two planes of symmetry, it is called the unsymmetrical substitutional center to distinguish it from the symmetrical substitutional mode. Strains are: two K⁺ ions, each by 0.26 Å, two K⁺ by 0.33 Å, five Cl⁻ by 0.20 Å; total, 2.2 Å.
center will be called the $C_{2v}$ negative center although it does not itself possess $C_{2v}$ symmetry. The minimum total strain is achieved when the sulfate ion is rotated on the twofold axis of the vacancy complex about 20° in either direction from the plane of the vacancies, as illustrated in Figure 9. Before rotation the center had two planes of symmetry, one a (100) plane and the other a (110) plane.

$C_{3v}$ Neutral Centers. A neutral center is obtained if the sulfate ion is incorporated in a vacancy complex consisting of three adjacent chloride ion vacancies in a (111) plane and the potassium ion vacancy which is nearest neighbor to all three. This vacancy complex possesses $C_{3v}$ symmetry. Two modes of incorporation are probable. The more symmetrical mode, shown in Figure 10, is called the symmetrical $C_{3v}$ neutral center. One of the four oxygen atoms of the sulfate ion is located in the potassium ion vacancy, and the other three O atoms are in the three chloride ion vacancies. In the hard-sphere approximation the sulfate ion has only about 0.03 Å freedom to move along the threefold axis, and essentially no freedom to liberate on this axis.

The most probable mode of reorientation of the sulfate ion occurs when the oxygen atom in the $K^+$ ion vacancy passes between two of the three restraining $Cl^-$ ions, straining each by 0.49 Å. Such reorientation gives rise to the second probable center, called the
The sulfate ion is located in a vacancy complex consisting of two \( \text{Cl}^- \) ion vacancies and a \( \text{K}^+ \) ion vacancy (dotted circles) and having \( C_{2v} \) symmetry. The center has an effective negative charge. Minimum total strain is achieved when the sulfate ion is rotated about the \( C_{2v} \) axis approximately 20° in either direction from the plane containing the vacancies. Four \( \text{Cl}^- \) ions are strained by 0.17 Å each, and two \( \text{Cl}^- \) by 0.25 Å, giving a total strain of 1.2 Å.
Fig. 10. - Sulfate ion in KCl: Symmetrical $C_{3v}$ neutral center

The sulfate ion is situated in a vacancy complex consisting of three adjacent chloride ion vacancies in a (111) plane and the potassium ion vacancy which is nearest neighbor to all three. (Vacancies are indicated by dotted circles). The neutral center has a $C_{3v}$ axis coinciding with the unit cell diagonal (dotted). The sulfate ion is held in position with essentially zero strain.
unsymmetrical $C_{3v}$ neutral center (Figure 11); the center, however, no longer possesses $C_{3v}$ symmetry. Two oxygen atoms are located in one of the three chloride ion vacancies, on a unit cell diagonal. The other two oxygen atoms extend somewhat into the remaining two Cl$^-$ ion vacancies, but lie about 0.5 Å out of the plane of the Cl$^-$ ion vacancies toward the K$^+$ ion vacancy.

The oxygen atom on the diagonal and farthest from the K$^+$ ion vacancy is not in contact with the host lattice. If positioning depended only upon repulsive interactions, this O atom would move in such a direction as to reduce the strain. However, such movement of the oxygen atom is electrostatically unfavorable, so the configuration of the center is believed to be approximately that described. The position of the sulfate ion is not as well defined as it is in the other centers which have been considered.

The Relative Importance of the Sulfate Ion Centers

The relative importance of any two of the sulfate ion centers is dependent on the Gibbs free energy change that occurs when one center in a crystal is replaced by the second. Evaluation of the free energy of a center is a very difficult exercise in lattice statics. The case of substitutional potassium ion in sodium chloride, which is simpler because it involves no long-range polarization of the crystal,
Fig. 11. - Sulfate ion in KCl: Unsymmetrical $C_{3v}$ neutral center

The sulfate ion is situated in a vacancy complex consisting of three adjacent Cl$^-$ ion vacancies in a (111) plane and the K$^+$ ion vacancy which is nearest neighbor to all three. Vacancies are indicated by dotted circles. Two of the oxygen atoms of the sulfate ion are located in one chloride ion vacancy and are on a diagonal (dotted) of the unit cell centered on that vacancy. The other two O atoms extend partially into the remaining two Cl$^-$ ion vacancies and slightly into the K$^+$ ion vacancy. Total strain is estimated at about 0.4 Å.
has been considered by Hardy (26). Fortunately, qualitative argument is sufficient to show that the predominant mode of incorporation is that of symmetrical substitution. Because symmetrical substitutional centers and negative ion vacancies bear opposite effective charges, they will associate at lower temperatures to form a neutral center which is denoted the neutral symmetrical substitutional center.

**Simple Substitution.** The symmetrical substitutional center and unsymmetrical substitutional center are similar in that each bears a net negative charge, and hence requires the incorporation of an equivalent number of negative ion vacancies. They differ only in the orientation of the sulfate ion in the negative ion vacancy. Distortion of the surrounding crystal is greater in the case of the unsymmetrical center; the respective total strains for the symmetrical and unsymmetrical centers are 0.7 Å and 2.0 Å. Therefore, the symmetrical center will exist in the crystal in higher concentration.

**Symmetrical Neutral Center.** The symmetrical neutral center may be formed by movement of a sulfate ion in a neutral symmetrical substitutional center to the position midway between the two chloride ion vacancies. The activation energy for diffusion of a chloride ion vacancy, 1.18 ev (24), is the energy required to bring a
negative ion vacancy to the position midway between two negative ion vacancies. Clearly, the energy required to bring the larger, doubly charged sulfate ion to the same point will be larger. Hence, the symmetrical neutral center cannot be present in the crystal in appreciable concentration.

**Interstitial Centers.** The interstitial centers may be formed by movement of a sulfate ion from its position in a symmetrical substitutional center to an interstitial site. The large distortion produced in the crystal is sufficient to render the concentration of such centers insignificant with respect to even the symmetrical neutral center.

**C$_{3v}$ Neutral Centers.** Formation of a symmetrical or unsymmetrical C$_{3v}$ neutral center may take place in the following steps: formation of a neutral vacancy pair, association of the pair with a neutral symmetrical substitutional center, and subsequent reorientation of the sulfate ion. The free energy change attending the association step cannot be very negative, since the entropy factor is positive, and the association of two neutral centers cannot be very exothermic. Formation of a neutral vacancy pair requires an energy somewhat in excess of 1 ev (11, p. 174). Therefore, the reorientation of the sulfate ion must be quite exothermic if the C$_{3v}$ neutral
centers are to be important.

One of the oxygen atoms of the sulfate ion in a symmetrical $C_{3v}$ neutral center is nearly centered in the potassium ion vacancy of the center. Such placement of a negatively charged oxygen atom is quite unfavorable electrostatically, and this center is therefore deemed unimportant.

Before reorientation to give the unsymmetrical $C_{3v}$ neutral center, the sulfate ion is in contact with five potassium ions and no chloride ions. After reorientation, the sulfate ion is in contact with four potassium ions and three chloride ions. The reorientation is probably endothermic; it is quite unlikely that it would be sufficiently exothermic to render negative the standard free energy of formation of the unsymmetrical $C_{3v}$ neutral center. It is therefore improbable that this center is present in potassium chloride in appreciable concentration.

$C_{2v}$ Negative Center. The $C_{2v}$ negative center may be considered as a dissociation product of a $C_{3v}$ neutral center. The dissociation is quite endothermic in that it involves charge separation and also forces the sulfate ion quite deeply into the potassium ion vacancy. Hence, it is probably of even less significance than the $C_{3v}$ neutral centers.
Summary. The probable modes of incorporation of the sulfate ion in potassium chloride have been considered. The predominant mode of incorporation has been shown to be symmetrical substitution. The unsymmetrical substitutional mode is probably second in importance.
ASSOCIATIONS OF SULFATE ION IN POTASSIUM CHLORIDE

General

The infrared absorption spectra of sulfates have been investigated in powder films (35, p. 1497), in Nujol mulls (48, p. 1276-1278), and in alkali halide pellets (47). The triply degenerate asymmetric stretching mode of the sulfate ion occurs at a frequency of about 1100 cm$^{-1}$; the symmetric stretch is inactive, and occurs at approximately 1000 cm$^{-1}$. Meloche and Kalbus (47) noted that potassium bromide and potassium chloride pellets containing copper sulfate give some additional bands on standing, and attributed these bands to the exchange of anions between the alkali halide and the copper sulfate. Lawson and Barnett (44) quenched melts of potassium bromide containing potassium sulfate, and made pellets from this material. The half width of the asymmetric stretching band was reduced to about 50 cm$^{-1}$, the most striking change being the elimination of the long sloping sides of the band which were observed in pellets prepared without fusion of the salt mixture. The symmetric stretch was sufficiently perturbed to be active, and was observed at a frequency of slightly less than 1000 cm$^{-1}$.

While the infrared spectra of other polyatomic anions in single crystals have been observed (46, 72), sulfates had not previously
been so investigated. The present work has been concerned with the spectra of potassium chloride single crystals containing potassium sulfate and of crystals containing both potassium sulfate and a divalent metal chloride. The divalent cations were found to associate with the sulfate ion, and to remove the degeneracy of the asymmetric stretching mode by perturbing the symmetry of the sulfate ion. The general nature of the perturbation was observed to be the same for each of the perturbing divalent cations, and the magnitudes of perturbation were similar. The degeneracy of the asymmetric stretching mode also disappeared in the crystals doped only with potassium sulfate, indicating sulfate ion to be present in an unsymmetrical environment. The ultraviolet as well as infrared spectra of crystals containing both lead chloride and potassium sulfate denoted association of the lead ion with the sulfate ion.

**Experimental Procedures**

Potassium chloride single crystals for the investigation were grown in the author's apparatus using the method described in the previous section. The concentration of doping in the melt varied between 1-4 mg of doping salt per gram of potassium chloride.

Infrared absorption spectra of the crystals were recorded using a Perkin-Elmer model 21 infrared spectrophotometer at a spectral
Fig. 12.—The infrared spectrum of KCl (Mg$$^{2+}$$, SO$$^-_4$$)
Fig. 13.—The infrared spectrum of KCl(Ca^{++}, SO_{4}^{--})
slit width of about 5 cm\(^{-1}\). The spectra of crystals containing both sulfate ion and a divalent cation were carefully reinvestigated with a Beckman model IR-7 spectrophotometer at approximately 1 cm\(^{-1}\) spectral slit width. The path length ranged from 2-4 cm, and the concentration of sulfate ion in the path was of the order of 0.1 µM/cm\(^2\).

**Association of the Sulfate Ion with Divalent Cations**

**Experimental Results**

**Infrared Spectra**

Examples of the spectra of potassium chloride crystals doped with magnesium, calcium, lead and barium sulfates are shown in Figures 12, 13, 14 and 15, respectively.\(^1\) In each case the symmetric stretching mode of the sulfate ion has been perturbed sufficiently to give rise to a weak absorption band at about 1000 cm\(^{-1}\), which will be called the \(\beta_1\) band. The degeneracy of the asymmetric stretching mode has been removed. The three bands grouped around 1140 cm\(^{-1}\) will be referred to in order of increasing frequency as the \(\beta_2', \beta_3\) and \(\beta_4\) bands. The additional band, present in the spectrum

\(^1\) In the figures, and elsewhere when symbols are used, the use of parentheses is adopted to indicate the nature of doping. For example, KCl(K\(_2\)SO\(_4\)) denotes a KCl crystal containing a small amount of K\(_2\)SO\(_4\), and the expression KCl(Mg\(^{++}\), SO\(_{4}^{--}\)) indicates that small amounts of MgCl\(_2\) and K\(_2\)SO\(_4\) have been added to the KCl melt.
Fig. 14.—The infrared spectrum of KCl(Pb^{++},SO_4^{--})
Fig. 15. - The infrared spectrum of $\text{KCl}(\text{Ba}^{++},\text{SO}_4^{--})$ following heat treatment.
of the crystal doped with magnesium sulfate at 1135 cm\(^{-1}\), is designated by a. Isotopic peaks due to \(^{34}\)S may be observed.

The Effect of Heat Treatments on the Infrared Spectra

Heat treatments of the crystal doped with magnesium sulfate indicated that the alpha band arises as a result of thermal dissociation of the species giving rise to the beta bands. Rapid cooling from 500\(^\circ\)C enhanced the \(\alpha\) band with respect to the \(\beta\) bands, while annealing at 265\(^\circ\)C led to the near extinction of the \(\alpha\) band and growth of the \(\beta\) bands, as shown in Figure 16.

The crystal containing barium sulfate, as grown, gave an anomalous spectrum (Figure 17) which was observed to change with time. The expected spectrum (Figure 15), containing only the beta bands, was obtained after annealing the crystal overnight at 350\(^\circ\)C. In addition to a prominent alpha band, the anomalous spectrum contains a composite band at a frequency slightly greater than 1200 cm\(^{-1}\). This composite band was observed to decrease with time at room temperature and also to change in shape.

The Ultraviolet Spectrum of Crystals Containing Divalent Lead

A divalent cation proved to be present in some crystals intentionally doped only with potassium sulfate. The position of the
Fig. 16. - The infrared spectrum of KCl(Mg$^{++}$, SO$_4^{--}$) on quenching from (a) 500°C (b) 265°C.
Fig. 17.- The infrared spectrum of KCl(Ba$^{++}$,SO$_4^{--}$) prior to heat treatment.
infrared beta bands indicated that the impurity was lead. As the
presence of lead (II) ion in potassium chloride leads to absorption
in the ultraviolet region at 273 m\(\mu\) (34, p. 865 & 869), confirmation of the identity of the impurity was sought by investigation of the ultraviolet spectrum of one of these crystals. The spectrum was found to contain not only a peak at 272 m\(\mu\), but an additional peak at 249 m\(\mu\), as shown in Figure 18. Heating the crystal in a tube furnace in air led first to an increase in the 272 m\(\mu\) band at the expense of the 249 m\(\mu\) band, and then to a decrease in both bands. However, when the crystal was placed in a Pyrex capsule containing chlorine gas and the capsule was air-quenched from different temperatures, the conversion between the two bands proved to be reversible. The 249 m\(\mu\) band is associated with PbSO\(_4\) ion pairs.

**Oscillator Strengths of the Alpha and Beta Bands**

Oscillator strengths of the alpha and beta bands could not be calculated from the melt concentration of the doping agent and the distribution coefficient for sulfate ion between melt and crystal which was determined using potassium sulfate as the doping agent. The difficulty arose from the effect of divalent cations on the distribution coefficient.

The optical density of a crystal grown from a melt containing
1.0 mg K$_2$SO$_4$ and 4.0 mg CaCl$_2$ per g KCl was compared to that of a crystal grown from a melt containing 2.5 mg K$_2$SO$_4$ and 0.2 mg CaCl$_2$ per g KCl, at the wavelength of the $\beta_4$ band. The distribution coefficient in the former case was found to be approximately twice that in the latter; an increased concentration of divalent cations in the melt enhances the solubility of sulfate ion in potassium chloride.

**Discussion of Results**

**Dispersion of MSO$_4$ Ion Pairs in Potassium Chloride**

The half-width of the infrared absorption bands observed in the clear single crystals varied in the range 10-20 cm$^{-1}$. However, when the crystals were cloudy due to internally precipitated sulfates, the bands were wider and the spectra began to take on the character of those obtained from mulls or pellets. Because of this difference, it is felt certain that the sulfates are present in solid solution in clear crystals; that is, the sulfates are dispersed as isolated metal-sulfate ion pairs.

**Origin of the Alpha Band**

Because the solubility of each of the divalent metal chlorides in potassium chloride crystals is much greater than that of potassium sulfate, the divalent cation concentration much exceeded the
sulfate ion concentration in most of the crystals investigated. However, in the case of the crystal doped with magnesium sulfate, it is believed that most of the magnesium ion was precipitated as the oxide, due to the presence of a small amount of water in the salt or in the nitrogen atmosphere in which the crystal was grown, and that the concentration of the divalent cation was much lower in this case than in the others. The low concentration would favor dissociation of the pair composed of the sulfate ion and divalent cation (MgSO₄ pair).

The change in the spectrum of the magnesium sulfate-doped crystal induced by heat treatments (Figure 16) make it clear that the alpha band is to be associated with the isolated sulfate ion. Since the degeneracy of the asymmetric stretching mode of the sulfate ion is not removed, it is also clear that dissociation of the MgSO₄ ion pair leaves the sulfate ion in an environment of cubic symmetry. The alpha band is therefore associated with the symmetrically substituted sulfate ion, which was shown schematically in Figure 7.

**Origin of the Beta Bands**

The divalent cation in an MgSO₄ pair may be assumed to have replaced a potassium ion at the cube face center of the unit cell containing the symmetrically substituted sulfate ion, as this is the
Fig. 18.—The ultraviolet spectrum of KCl(Pb$^{2+}$,SO$_4^{2-}$)
position of closest approach. The effective symmetry of the center is then $C_{2v}$, and the degeneracy of the asymmetric stretch is completely removed.

The presence of the divalent cation will cause polarization of the sulfate ion. From the viewpoint of resonance structures of the sulfate ion, the favored structure is that in which the two oxygen atoms adjacent to the divalent cation carry a negative charge and the two opposite oxygen atoms are bonded to the sulfur by double bonds.

A perturbation calculation was made by J.C. Decius in which it was assumed that changes in the force constants of the sulfur-oxygen bonds are equal, but opposite in sign. The result obtained with $\lambda = 4\pi c^2 \omega^2$ is given by

$$
\begin{vmatrix}
\lambda_1^o - \lambda & -G_1 \Delta f \\
-G_2 \Delta f & \lambda_2^o - \lambda
\end{vmatrix} = 0 \text{ (for } \lambda = \lambda_1, \lambda_3)$$

$$\lambda_2 = \lambda_2^o - G_1 \Delta f$$

$$\lambda_4 = \lambda_2^o + G_1 \Delta f$$

where $\lambda_1^o$ is for the totally symmetric mode, $\lambda_2^o$ is for the triply degenerate mode, $G_1$ and $G_2$ are the respective $G$ matrix elements in

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$^2/$ Decius, J.C., Professor of Chemistry. Oregon State University, Corvallis, Oregon.
symmetry coordinates, \( \Delta f \) is the change in force constant of a sulfur-oxygen bond, and zero superscripts indicate unperturbed values. The results of the calculation are shown in Table 3, where the calculated frequencies are compared with those observed. The frequency \( \omega_1 \) corresponds to the \( \beta_1 \) band, \( \omega_2 \) to the \( \beta_2 \) band, and so forth.

Table 3. Observed \( \text{SO}_4^2- \) Stretching Frequencies (cm\(^{-1}\)) Compared with Calculated Values for Adjacent M\(^{2+}\)(C\(_{2v}\))

<table>
<thead>
<tr>
<th></th>
<th>MgSO(_4)</th>
<th>CaSO(_4)</th>
<th>BaSO(_4)</th>
<th>PbSO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_1 )</td>
<td>978.5</td>
<td>978.5</td>
<td>982</td>
<td>980</td>
</tr>
<tr>
<td>( \omega_2 )</td>
<td>1083.5</td>
<td>1084</td>
<td>1089</td>
<td>1086</td>
</tr>
<tr>
<td>( \omega_3 )</td>
<td>1149</td>
<td>1148</td>
<td>1157</td>
<td>1150</td>
</tr>
<tr>
<td>( \omega_4 )</td>
<td>1188</td>
<td>1188</td>
<td>1185.5</td>
<td>1188</td>
</tr>
</tbody>
</table>

The values of the unperturbed frequencies should be the same in all cases; this is seen to be approximately true except in the case of lead, where covalency is undoubtedly a factor. The agreement between observed and calculated frequencies, and the constancy of the parameters \( \omega_1^0 \) and \( \omega_2^0 \), are more than satisfactory in view of the simplicity of the potential energy model, which neglects the changes induced in the bond-bond coupling force constants by the divalent cation, and which, as noted above, assumes that the softening of the \( \text{S-O}^- \) bonds is equal to the stiffening of the \( \text{S}=\text{O} \) bonds. Using the
unperturbed frequencies for the salts MgSO$_4$, CaSO$_4$ and BaSO$_4$ and neglecting the coupling with the bending modes, one finds $f = 7.79$ mdyne/Å and $f' = 0.50$ mdyne/Å, the latter being of the same order as the observed changes in $f$.

**Origin of Anomalous Bands of KCl(Ba$^{++}$, SO$_4^{--}$)**

The prominent alpha band in the anomalous spectrum of the crystal doped with barium sulfate (Figure 17) is believed to be associated with the anomalous band at 1205 cm$^{-1}$ rather than with the isolated symmetrically substituted sulfate ion. The perturbation indicates that the barium ion is near three oxygen atoms on the threefold axis. With the barium ion in this position, there would be only two-fold splitting. Three sulfur-oxygen bonds would be weakened, and the bond opposite the barium ion would be strengthened to a greater extent than would the two SO bonds opposite the barium ion in the case of C$_2$v association. Since the shape of the anomalous bands changes with time, there must be two centers in which the barium ion is located near the threefold axis. If there were only one center, it would seem reasonable to suggest that the irregular absorption be accounted for by a barium ion located at the corner rather than at the face-center position of the unit cell containing the symmetrically substituted sulfate ion. However, the observed perturbation appears
too large for this charge separation.

The only possible explanation for the anomalous absorption is afforded by association of the barium ion with the unsymmetrically substituted sulfate ion, as shown in Figure 19. The barium ion is quite near the threefold axis when located in one of the face-center positions numbered (1) or (2) on the diagram. It is suggested that the barium ion and sulfate ion are already associated when incorporated into the crystal.

Approximate calculations indicate that the degree of dissociation of BaSO$_4$ ion pairs in the melt is very small. In the melt, the barium ion would assume a position nearest the center of charge of the sulfate ion, which is on a threefold axis. While this association must occur with the other divalent cations, barium is the largest divalent cation excepting radium; therefore rearrangement to the C$_{2v}$ center occurs with greater difficulty following incorporation into the crystal.

The Equilibrium Constant for Dissociation of MSO$_4$ Ion Pairs

Association of divalent cations and divalent anions is to be expected since each bears an excess charge. The equilibrium constant for the reaction

$$\text{MSO}_4 \rightleftharpoons M^{++} + \text{SO}_4^{--}$$
Fig. 19.- Barium ion associations with the unsymmetrical substitutional center

The barium ion, if substituted for a potassium ion in one of the face-center positions of type (1) or (2), would be very near to the threefold axis of the sulfate ion.
may be obtained by setting the variation in the free energy of the crystal, with the extent of the reaction, equal to zero.

The enthalpy change for the reaction at zero pressure is

$$\Delta H = \frac{n e^2}{\epsilon r}$$

where \(e\) is the electronic charge, \(r\) the charge separation in the associated ion pair, and \(\epsilon\) the static dielectric constant of potassium chloride. It is assumed that long-range forces acting between the dissociated ions are negligible. The equilibrium constant obtained is therefore valid only at low concentrations of the metal sulfate.

The entropy change for the dissociation is given by the expression

$$\Delta S = n \Delta S_v + n \Delta S_c$$

in which \(\Delta S_v\) is the entropy change of the crystal per dissociating ion pair which arises from small changes in the vibrational modes of the crystal. \(\Delta S_c\) is the configurational entropy change per dissociating ion pair; it is calculated from the Boltzmann-Planck equation \(S = k \ln W\), where \(W\) is the number of different ways of obtaining a given macroscopic state.

If there are \(N\) lattice sites of one sign per \(\text{cm}^3\) in potassium chloride, there are \(N!\) permutations of the divalent and monovalent ions. However, permutations of like ions do not increase the thermodynamic probability of a state; therefore
\[ W_{(M^{++})} = W_{(SO_4^{--})} = \frac{N!}{(N-n)! \, n!} \]

and

\[ S_{c(M^{++})} = S_{c(SO_4^{--})} = k \ln \left( \frac{N!}{n! \, (N-n)!} \right) \]

When associated with a divalent cation, the sulfate ion has been shown to be incorporated into potassium chloride substitutionally for the chloride ion. The divalent cation is in the nearest-neighbor position, and the four oxygen atoms of the sulfate ion are each directed along a diagonal of the unit cell. The thermodynamic probability associated with a potassium chloride crystal containing \( N \) positive and \( N \) negative ions per \( \text{cm}^3 \), of which \( 2m \) are paired divalent ions, is

\[ W_{(\text{KCl})} = \frac{6^m N!}{m! \, (N-m)!} \]

The factor \( 6^m \) appears because of the six possible pairs which may be associated with any given lattice point. The configurational entropy is given by

\[ S = k \ln \left( \frac{6^m N!}{m! \, (N-m)!} \right) . \]

If the total concentration of \( \text{MSO}_4 \) is \( a \), then \( m = a-n \), and the configurational entropy change for the reaction may be represented as

\[ \Delta S_c = 2k \ln \left( \frac{N!}{n! \, (N-n)!} \right) - k \ln \left( \frac{6^{(a-n)} N!}{(a-n)! \, (N-a+m)!} \right) . \]
Use of the Stirling approximation and the fact that \( m \) and \( n \) are much smaller than \( N \) leads to the expression

\[
\Delta S = 2n k \ln \left( \frac{N}{n} \right) - (a-n) k \ln \left( \frac{N}{a-n} \right)
\]

The expression for the free energy change is then

\[
\Delta F = \frac{ne^2}{\epsilon r} - nT \Delta S - 2n kT \ln \left( \frac{N}{n} \right) + (a-n) k \ln \left( \frac{N}{a-n} \right)
\]

Solution of \( \frac{\partial F}{\partial n} = 0 \) yields the result

\[
\frac{2}{a-n} = \frac{N}{6} \exp \left( \frac{\Delta S}{k} \right) \exp \left( -\frac{e^2}{\epsilon r k T} \right)
\]

or

\[
\frac{[M^{++}][SO_4^{--}]}{[MSO_4^4]} = \frac{N}{6} \exp \left( \frac{\Delta S}{k} \right) \exp \left( -\frac{e^2}{\epsilon r k T} \right)
\]

The value of the vibrational entropy term is best discussed in terms of the Einstein model of the crystal. The vibrational entropy for each mode of vibration is obtained from the equation

\[
S_v = \frac{k}{\nu} - k \ln \left( \frac{e^x}{e^x - 1} \right)
\]

where \( x = h\nu/kT \). When \( x \) is small, \( S_v \) reduces to \( k(1 - \ln x) \). Though the value of \( x \) is about \( 1/3 \) at a temperature of \( 600^\circ\text{K} \), the approximate equation is sufficiently accurate for purposes of this discussion.

When a divalent cation is substituted for a potassium ion in KCl, the six surrounding chloride ions experience repulsive forces when
moving toward the divalent cation which differ from those experienced when moving toward a potassium ion, and the Einstein frequency of these chloride ions for the modes of vibration along a line pointing toward the divalent cation is changed from $\nu_-$ to $\nu'_-$. This changes the vibrational entropy of the crystal by an amount

$$6k \ln \left( \frac{\nu'_-}{\nu_-} \right).$$

The divalent cation in the crystal has an Einstein frequency differing from that of the potassium ion for which it has been substituted, and will contribute a term

$$3k \ln \left( \frac{\nu'_{++}}{\nu'_+} \right).$$

Analogous terms give the vibrational entropy change attending incorporation of the sulfate ion.

If it is assumed that on association of a divalent cation and a sulfate ion, the frequency of one of the vibrational modes of the divalent cation shifts from $\nu_{++}$ to $\nu'_{++}$; that the frequency of one of the vibrational modes of the sulfate ion (not internal) shifts from $\nu_-$ to $\nu'_-$, and that the five chloride and five potassium ions adjacent to the ion pair undergo a shift in vibrational frequency of a mode from $\nu'_-$ and $\nu'_+$ to $\nu''_-$ and $\nu''_+$, then the factor in the equilibrium constant arising from the vibrational entropy change attending dissociation of the MSO$_4$ ion pair is given by
$$\exp \left( \frac{\Delta S}{k} \right) = \left( \frac{\nu^+ \nu^-}{\nu''^+ \nu''^-} \right)^5 \left( \frac{\nu' \nu''}{\nu''^+ \nu''^-} \right)^5 \left( \frac{\nu' \nu''}{\nu''^+ \nu''^-} \right)^5$$

An idea of the magnitude of this factor is obtained by comparison to a similar term in the experimentally determined expression giving the equilibrium number of Schottky defects, \( n \), as a function of temperature and the enthalpy of formation of the defects, \( \phi \). The expression adapted from Etzel and Maurer (18) is

$$n = N \exp \left( \frac{\Delta S}{k} \right) \exp \left( -\frac{\phi}{2kT} \right) = 1.2 \times 10^{23} \exp \left( -\frac{\phi}{2kT} \right)$$

from which the vibrational entropy term is about 5. The perturbation of the vibrational spectrum of a potassium chloride crystal attending formation of a pair of Schottky defects is probably similar in magnitude to that attending incorporation of a divalent cation and a sulfate ion into the crystal. As association of a divalent cation and a sulfate ion will only partially reduce their perturbing influence, it seems reasonable to assume that the vibrational entropy term is nearer to 1 than to 5, and that it may be neglected in the calculation of the equilibrium constant.

To evaluate the enthalpy term in equation (1), it is necessary to specify the dielectric constant and the charge separation. The dielectric constant is a function of temperature, and a temperature of 600°K is arbitrarily chosen for this calculation. Eucken and Buchner (19, p. 344) gave a value of 4.68 ± 0.01 for the
low-frequency dielectric constant at room temperature, and a value of \(30.5 \times 10^{-5}\) for the expression \(d(\ln \epsilon)/dT\) in the range -100 to 100°C. Extrapolation to 600°C gives \(\epsilon = 5.13\). The value of \(\alpha\) is dependent on the identity of the divalent cation. It is the equilibrium constant for \(\text{CaSO}_4\) ion pairs which is calculated.

Polarization of the calcium and sulfate ions reduces the effective charge separation. Tessman and Kahn (75) reported the polarizability of sulfate ion in potassium sulfate to be \(4.8 \text{ Å}^3\), and that of calcium ion to be \(1.1 \text{ Å}^3\). The effective charge separation is thus less than the internuclear distance by the amount

\[
\frac{a_{\text{SO}_4^{--}} + a_{\text{Ca}^{++}}}{2\epsilon r^2} = 0.07 \text{ Å}.
\]

The calcium ion in a \(\text{CaSO}_4\) ion pair is located at the edge of the sulfate ion tetrahedron. The calcium-sulfur internuclear distance is 2.82 Å, assuming an oxygen radius of 1.36 Å and a calcium ion radius (Pauling) of 0.94 Å. The effective charge separation is therefore 2.75 Å. With \(\Delta H = 1.02\) ev, and omitting the vibrational entropy term, the equilibrium constant for dissociation of isolated calcium sulfate pairs at 600°C is

\[
\frac{[\text{Ca}^{++}][\text{SO}_4^{--}]}{[\text{CaSO}_4]} = 4 \times 10^{12}.
\]

Thus, if the total concentration of \(\text{CaSO}_4\) is \(10^{17} \text{ cm}^{-3}\), the degree of
dissociation is slightly under 1 percent.

The Use of Sulfate Ion to Determine Valence of Cations
Incorporated in Potassium Chloride Single Crystals

Since the magnitude of splitting of the sulfate ion asymmetric stretch did not vary greatly on perturbation with the four divalent cations studied, being chiefly an electrostatic effect, it would appear that the infrared spectra would indicate whether the valence of an impurity cation in potassium chloride were 1, 2 or 3.

Lidiard (45, p. 295-298) has investigated the stability of cations in potassium chloride with respect to reduction to the next lower oxidation state. He has shown that if the ionization potential associated with the removal of an electron from an atom or ion to yield a given oxidation state is greater than about 22 ev, the element will not exist as a substitutional impurity in the given oxidation state but in the lower one. Chromium has a second ionization potential of 16.6 ev, and therefore might be expected to be incorporated as chromium (II).

A portion of KCr(SO₄)₂·12H₂O was dried by heating it to 500°C in an evacuated Pyrex tube with one end immersed in liquid nitrogen. Using this material and potassium sulfate for doping the doubly re-crystallized potassium chloride, a crystal was grown under dry nitrogen in a platinum crucible. The concentration of divalent cations in the crystal was not sufficient to repress some of the bands which
appear in the spectra of crystals not doped with a divalent cation, but bands were observed at 1188, 1158 and 1084 cm\(^{-1}\) and were attributed to divalent chromium.

The third ionization potential of gadolinium is unknown, but Hills (33) was unable to detect the presence of gadolinium (III) in crystals grown from a melt doped with GdCl\(_3\). Reduction to the divalent state and the presence of the divalent ion in potassium chloride were indicated in a crystal grown from a melt doped with both gadolinium trichloride and potassium sulfate. The infrared spectrum of the crystal showed only the alpha band and asymmetric stretching bands at 1187, 1157 and 1092 cm\(^{-1}\).

A crystal was grown from a melt doped with potassium sulfate and with the residue obtained by drying a potassium chloroplatinate solution. After growth of this crystal, metallic platinum was found at the bottom of the melt. There was evidence, however, for the presence of platinum (II) in the crystal; weak absorptions were observed at 1187, 1158 and 1092 cm\(^{-1}\), though these absorptions were somewhat obscured by the presence of bands observed in crystals doped only with potassium sulfate. While the positions of the bands in the spectrum of the platinum-doped crystal coincide with those attributed to GdSO\(_4\) ion pairs, there was no possibility of cross-contamination as the platinum-doped
crystal was grown from a platinum crucible and the gadolinium-doped crystal was grown from one of porcelain.

Associations of Sulfate Ion in KCl(K₂SO₄)

General

When the general character of the spectra of crystals containing MSO₄ ion pairs had been established, and the alpha (1135 cm⁻¹) band had been identified as that arising from the symmetrically substituted sulfate ion, attention was directed toward crystals doped only with potassium sulfate. Special efforts were made to reduce the concentration of divalent cations to the point that the effect of these impurities would be unimportant. The observed absorption bands were not well resolved, and were superimposed on a broad, uneven absorption believed to be due to a colloidal dispersion of potassium sulfate.

Experimental

Growth of Pure Crystals

The concentration of sulfate ions in the potassium chloride crystals investigated is of the order of 10¹⁶ cm⁻³. In order to reduce the absorption due to MSO₄ ion pairs to 10 percent of the total
absorption, the divalent cation concentration must be in the magnitude of \(10^{15}\) ions/cm\(^3\), or in the 0.1 ppm range. To obtain this purity, crystals were grown from reagent grade potassium chloride which was first purified by the method of Hay (30) and then doubly recrystallized. Reagent grade potassium sulfate was doubly recrystallized before its use as the doping agent.

The apparatus constructed by Gruzensky (22, p. 12-15) for the production of high-purity single crystals was used for the growth of the crystals; they were grown from a crucible of high-purity graphite in an atmosphere of argon. The apparatus was not equipped with a rotating cold finger.

The Infrared Spectrum of KCl(K\(_2\)SO\(_4\)) As Grown

The spectrum of a crystal grown from a melt containing 1.9 mg K\(_2\)SO\(_4\) per g KCl may be seen in Figure 20, curve (a). Four prominent bands are observed, corresponding to frequencies of 1112 cm\(^{-1}\) and approximately 1130, 1160 and 1170 cm\(^{-1}\). These will be respectively called the \(\eta_1\), \(\eta_2\), \(\eta_3\) and \(\eta_4\) bands. The symmetrical shape of the \(\eta_1\) band is apparent. The other bands are not well resolved, and appear to be complex. However, their irregularities in shape may be due to the character of the underlying colloidal absorption. The colloidal absorption is referred to as such because
The infrared spectrum of a crystal grown from a melt containing 1.9 mg K₂SO₄ per g KCl is shown after the following successive treatments: (a) growth of crystal (b) 3 hr heat treatment at 600°C (c) overnight at 325°C and (d) 1 week at 110°C. Path length in (a) is greater than in (b)-(d).
the breadth and character of the absorption indicate that the sulfate ion is in a state which is much less well defined than if it were present in a simple absorption center such as an $\text{MSO}_4$ ion pair. Precipitation was not actually observed.

The Infrared Spectrum of $\text{KClK}_2\text{SO}_4$ Following Heat Treatment

The crystal described above was given two heat treatments in an evacuated Pyrex capsule, the first at $600^\circ\text{C}$ for 3 hr, and the second at $325^\circ\text{C}$ overnight. The capsule in each case was removed from the furnace and allowed to cool to room temperature without quenching. For a third heat treatment at $110^\circ\text{C}$ lasting one week, the crystal was not encapsulated. The spectrum following each treatment is shown in Figure 20. In comparing the curves it should be noted that the measurement of spectrum (a) involved a greater path length than was involved in the other curves; a portion of the crystal was cleaved away before beginning the heat treatments.

The relative intensities of the eta bands appear to vary, but this may be merely the result of a variation in the shape of the underlying colloidal absorption band. The latter band increased progressively with each heat treatment, at the expense of the eta bands.

The band at $1140\ \text{cm}^{-1}$ (designated the gamma band) was present in the spectrum of the crystal following the heat treatment.
at 600°C, but was absent following the treatments at 325 and 110°C. The gamma band appears to be narrower than others in the spectrum; this would indicate that the sulfate ion is held in a rather well-defined position in the center giving rise to the absorption at 1140 cm⁻¹.

Repression of Colloid Formation by Divalent Cations

During preliminary experiments, it was found that the center or centers responsible for the eta bands were stabilized in a crystal containing a small amount of some divalent cation. The spectrum of one such crystal, which was grown in the author's apparatus, is shown in Figure 21 (a). The presence of a small amount of intentionally added magnesium ion is evidenced by the peak at 1187 cm⁻¹; the absorption at 1197 cm⁻¹ indicates that a small amount of divalent lead is also present. The central asymmetric stretching bands (ν₃) due to MgSO₄ and PbSO₄ ion pairs are located at 1149 and 1150 cm⁻¹, respectively, and give only a barely observable peak. Except for the alpha (1135 cm⁻¹) band, the remainder of the spectrum is similar to that of KCl(K₂SO₄) prior to heat treatment, which was shown in Figure 20 (a).

The sulfate-doped crystal containing small amounts of magnesium and lead was subjected to three heat treatments of several
Fig. 21.—The effect of thermal treatment on KCl(K₂SO₄) containing small amounts of Mg⁺⁺ and Pb⁺⁺.

The infrared spectrum is shown of the crystal (a) as grown and (b) after several hours at 500°C.
hours each at approximately 500°C in an open Pyrex tube in a tube furnace. After each treatment the crystal was air-quenched with an air jet as rapidly as possible without causing the crystal to shatter. The spectrum following the third heat treatment is seen from Figure 21 (b) to have a somewhat enhanced alpha band, but it is otherwise very similar to the spectrum of the crystal as grown. The effect of the presence of a small concentration of divalent cations is to repress the formation of colloid.

Evidence for Diffusion of the Sulfate Ion

As the concentration of divalent cations in a crystal containing potassium sulfate is increased, the crystal must eventually become unstable with respect to precipitation of $\text{MSO}_4$. A crystal whose spectrum (Figures 15 and 17) has already been discussed was grown from a melt containing 2.5 mg $\text{BaSO}_4$ per g KCl. The crystal was initially free of precipitation, as indicated by its optical clarity, but upon heating at 350°C the crystal became opalescent. The broad absorption band upon which the beta bands are superimposed in the spectrum of the crystal following heat treatment (Figure 15) indicates that the precipitate was probably barium sulfate; the absorption occurred at lower energy than that of potassium sulfate. Since precipitation of the barium sulfate necessarily
involves diffusion of the sulfate ion, the sulfate ion must be mobile at temperatures above 350°C.

The crystals doped only with potassium sulfate were grown from melts having a potassium sulfate concentration almost as great as that producing cloudy crystals (due to precipitation of potassium sulfate on the crystal-melt interface). It was to be expected that these crystals would be unstable with respect to precipitation of potassium sulfate at temperatures much below the melting point of potassium chloride. The enhancement of colloidal absorption occurring on heat treatment of the crystals supports this contention, and is evidence for diffusion of the sulfate ion.

Possible Explanations for the Existence of Four Eta Bands

On the basis of previous qualitative argument, the centers whose presence is to be expected in KCl(K2SO4) are the symmetrical substitutional (alpha) center and the neutral center derived from association of the alpha center with a negative ion vacancy. If such were indeed the case, the alpha band and three other asymmetric stretching bands should be observed. Instead, four prominent (eta) bands occur in the spectrum of KCl(K2SO4), and none of these may be identified with the alpha band. Three explanations are considered for the existence of these bands: perturbation of the sulfate
ion by adjacent potassium and chloride ions, the presence of two
simple centers in similar concentration, and the existence of cen-
ters involving more than one sulfate ion.

**Interaction of Adjacent Ions with the Sulfate Ion**

More than three absorption bands could arise if there were sig-
nificant interaction of the stretching vibrations of the sulfate ion with
the optical vibrational modes of the potassium chloride crystal. For
such to be the case, the force constant associated with the optical vi-
bration of highest frequency in potassium chloride would have to be
similar in magnitude to those associated with the stretching vibra-
tions of the sulfate ion.

The Restrahl absorption of potassium chloride is at 140 cm\(^{-1}\),
while the absorption of the sulfate ion is at 1135 cm\(^{-1}\). The vibra-
tional frequencies thus differ by a factor of eight. Since vibrational
frequencies depend on the square root of the force constants, the
force constant governing the optical vibration of the ions in potassi-
um chloride is only 1 or 2 percent as large as the force constant of a
sulfur-oxygen bond. Divalent cations were found to induce a change
of about 10 percent in the force constant of the sulfur-oxygen bond of
the sulfate ion, and the associated frequency shift was about 50 cm\(^{-1}\).
If an ion adjacent to the sulfate ion were to move in a manner which
always opposed the motion of one of the oxygen atoms, it could do no more than shift the asymmetric stretch by 5 or 10 cm$^{-1}$. As such a phase relationship is impossible, the four eta bands, whose maxima are separated by at least 10 cm$^{-1}$, cannot be accounted for by interaction of potassium and chloride ions with the sulfate ion.

**The Presence of Two Simple Centers in Nearly Equal Concentration**

The presence of the four eta bands might be accounted for by two sulfate ion centers of approximately equal concentration. It will be recalled that the anomalous absorption bands in the spectrum of KCl(Ba$^{++}$, SO$_4^{--}$) were attributed to ion pairs involving the unsymmetrically substituted sulfate ion. If one accepts the possibility that metastable unsymmetrical substitutional sulfate ion centers may occur in KCl(K$_2$SO$_4$), he has at his disposal not only the unsymmetrical substitutional center itself, but the five neutral centers (Figure 22) derived by association of the center with a negative ion vacancy.

However, this explanation is untenable in view of the disappearance of the anomalous absorption bands in the spectrum of KCl(Ba$^{++}$, SO$_4^{--}$) on overnight heat treatment at $350^0$C. The eta bands were still prominent after the $600^0$C heat treatment of KCl(K$_2$SO$_4$). If divalent cations are required to catalyze the reorientation of the sulfate ion, these were present in the crystal containing small amounts
Fig. 22. - Modes of association of a negative ion vacancy with the unsymmetrical substitutional center.

Five different modes of association of a negative ion vacancy with the unsymmetrical substitutional center are possible; each is obtained by removal of one of the chloride ions numbered 1, 2, 3, 4, or 5.
of lead and magnesium ions. The eta bands of this crystal were not reduced by heat treatment at 500°C for several hours.

Association of Two or More Sulfate Ions:

Only those centers involving a single sulfate ion have been considered to this point. In view of the formation of colloidal potassium sulfate, it is clear that multiple centers involving two or three sulfate ions must have at least a transient existence. A multiple center would give rise to more than three absorption bands if it were not symmetrical with respect to the sulfate ions. Even if a center has symmetry such that all sulfate ions in the center absorb identically, a fourth absorption band might occur as a result of interaction between the sulfate ions. Hence, the four eta bands may result from one or more multiple centers.

The breadth of the eta bands makes it unlikely that any of these bands arises from the neutral symmetrical substitutional center (alpha center associated with a negative ion vacancy). The absorption bands arising from a multiple center may be broadened by interaction of the sulfate ions in the center, but the simple centers should have absorption bands similar in half-width to the alpha and beta bands.
Summary

Potassium chloride crystals grown from melts containing about 2 mg of potassium sulfate per gram of potassium chloride are unstable with respect to formation of colloidal potassium sulfate. Superimposed on the colloidal band of the spectrum of such crystals are four prominent bands which are believed due to one or more multiple sulfate ion centers. Rapid cooling of the crystals leads to a narrow absorption band at 1140 cm\(^{-1}\) which may be due to a simple center. A small concentration of divalent cations inhibits the formation of colloid.
THE COLOR CENTER BEHAVIOR OF POTASSIUM CHLORIDE CRYSTALS

General

The interactions of electrons with point defects in alkali halides has been a subject of intensive study and research during the past two decades. The identity of the defects responsible for the observed absorption bands is still in doubt or is unknown in many cases, and continued research interest in color centers is assured due to the variety, difficulty and fundamental nature of the problems involved. The two most extensive reviews of the field have been written by Seitz (69, 70).

Electrons may be made available to the point defects in a crystal by several means. For example, rock salt is sometimes found to be colored by natural radioactivity (63). Alkali halides are often colored by subjecting the crystals to x-ray irradiation (69, p. 384-385), but this procedure does not result in uniform distribution of color centers. Additive coloration produces quite uniform coloration, and is accomplished by heating the crystal in a closed capsule in the presence of the alkali metal vapor.

The method of additive coloration has been used in this work. The mechanism of the coloring process involves ionization of alkali metal atoms on the crystal surface. Diffusion of electrons into the body of the crystal probably occurs along disordered
interfaces at low temperatures and by means of vacancy pairs at high temperatures (50). Halide ions migrate to internal and then to external surfaces to prevent the formation of a space charge. If the crystal is rapidly cooled to room temperature after coloring, a single, symmetrical band called the F band is produced in or near the visible region. The F band is bleached by irradiation with light of the same wave length. Figure 23 shows the effect of such irradiation on an additively colored potassium chloride crystal at room temperature and indicates the letters used to designate the absorption bands which are produced under these conditions.

Incorporation of impurities into a crystal introduces additional electronic energy levels which may give rise to color centers. Multivalent impurities must introduce vacancies into a crystal to preserve electroneutrality, and addition of vacancies can have a market effect on the color center behavior of a crystal. For example, alkaline-earth metal ions, which introduce an equivalent number of positive ion vacancies, have been found to greatly enhance the rate of additive coloration of potassium chloride (61, p. 75). Shimizu reported that additively colored crystals containing sulfate ion are bleached thermally at a lower rate than are undoped crystals (71).

When potassium chloride crystals containing sulfate ion
Fig. 23. - Absorption bands of additively colored KCl
were colored and then bleached with F light, their spectra were found to differ from those of undoped potassium chloride crystals given similar treatment. The most obvious differences were noted in the M- and N-band regions. Since the behavior of the N bands had not been elucidated, a short investigation of these bands was necessary in order that comparisons could be made between doped and undoped crystals. Though based on limited observation, several important results were obtained from this study and will be presented prior to discussion of the color center behavior of crystals containing sulfate ion.

**Experimental Procedures**

**Coloring**

Additive coloration of a crystal was accomplished by heating the crystal with potassium metal in an evacuated Pyrex capsule. The coloring apparatus consisted of a vertical tube furnace of two abutted sections, each section controlled by a variable transformer. Thermocouples were used as temperature-sensing devices.

For convenience, the potassium metal was melted in a test tube in air and was drawn into Pyrex tubing of 8 mm inside diameter. One or two inches of the metal in this tubing was sufficient to
maintain a reservoir of liquid metal throughout the coloration. To prepare the coloring capsule, one end of a piece of Pyrex tubing having an inside diameter of 18 mm was sealed and a constriction was made about four inches from the sealed end to support the crystal. Through this construction was dropped a piece of the 8-mm tubing containing potassium metal. The crystal was next inserted into the capsule and another constriction was made in the tubing above the crystal, leaving only a small opening. The open end of the tubing was connected to a vacuum pump, and the capsule was sealed at the constriction while being held at a pressure of 50\(\mu\) or less.

The portion of the capsule containing the crystal was placed in the upper section of the coloring furnace and was kept at a temperature of approximately 600\(^\circ\)C, while the potassium in the lower section was held at temperatures varying from 325 to 450\(^\circ\)C, depending on the desired intensity of color. The concentration of F centers produced in this process is chiefly dependent upon the vapor pressure of the metal. One day was considered sufficient to produce uniform coloration, though crystals were usually left in the coloring furnace for at least two days.

After its removal from the coloring furnace, the capsule was immediately placed in a tube of aluminum foil and immersed
in carbon tetrachloride for rapid cooling. The crystal was then removed by breaking the capsule. Outer surfaces of the crystal were cleaved away with a razor blade to expose the inner portions whose properties were investigated.

Measurement of Absorption Spectra

A Beckman model DK-1 recording spectrophotometer was used to measure the absorption spectra of the crystals, and was also utilized as the light source for optical bleaching. It was adopted as standard bleaching procedure to set the slit width at 2.0 mm and to prevent rotation of the mirror which alternately directs light through the sample and reference paths, so that a steady rather than chopped bleaching light was obtained. All bleaching was carried out at room temperature. The intensity of the light source at 550 mµ was determined by Woodley\(^3\) to be

\[1.8 \times 10^{12} \text{ photons mm}^{-2} \text{ sec}^{-1}\].

The determination was made by measuring the current from a thermopile, which was calibrated using a standard white light source obtained from the National Bureau of Standards.

To enhance resolution of the absorption peaks, all spectra were measured at liquid nitrogen temperature (80°K) in a specially

constructed Dewar vessel. The crystal was fixed in a metal holder in an evacuable compartment with silica windows, the holder forming the bottom of the liquid nitrogen well. The cradle for the Dewar cell replaced the lid of the sample compartment of the spectrophotometer, and was painted flat black as well as felted to eliminate stray light from the compartment. The Dewar cell was evacuated to a pressure of 1 µ. To prevent frosting of the silica windows, a small jet of dry air was directed upon them. The crystal temperature was assumed to be that of the liquid nitrogen.

N-Center Reactions in Potassium Chloride Crystals

General

Prolonged bleaching of colored potassium chloride crystals with F light at room temperature leads to the formation of a broad, irregular absorption band of relatively low intensity in the 1000-µm region. This band was reported in 1949 by Burstein and Oberly (6), who designated it by the letter N. In earlier color center studies the N band was neglected, as attention was directed primarily toward the F, M and R bands. However, in 1956 Herman, Wallis and Wallis (31) noted that F-light irradiation causes the N band to shift toward the red portion of the spectrum. On the basis of this variation in shape, they asserted that there must be more than
one N band. Tomiki (77, p. 493) reported in 1960 that thermal
destruction of the R bands leads to the growth of the \( N_1 \) band,
although he did not distinguish the \( N_1 \) from the \( N_2 \) band which is
located at a greater wavelength. Hattori (27) has determined the
positions of the N bands in various alkali halides and has found that
Ivey's relation is obeyed; that is, the wavelength of maximum ab-
sorption varies linearly with the lattice constant.

As a model for the \( N_1 \) center, Pick (60) has suggested a
planar association of four F centers, the centers forming a dia-
mond in the (111) plane. His proposal for the \( N_2 \) center is a tetra-
hedral association of four F centers.

The present work confirms the observation of Herman,
Wallis and Wallis, and of Tomiki. Additional color center reac-
tions involving the N bands are presented, and models for the N
centers are proposed which differ from those of Pick. Hattori, in
a very recent paper (28), has confirmed nearly all of the observa-
tions of the author, but has not tried to explain the observations in
terms of color center models and reaction mechanisms to the extent
attempted here.

Experimental

Purity of Crystals

For investigation of the N bands, two undoped potassium
chloride crystals were used. Crystal A was grown by Gruzensky during a study of methods for preparation of high-purity crystals. Gruzensky (22, p. 12-15, 69&73) has described the preparation and purity of the crystal, to which he assigned the number G-43. The ionic conductivity of the uncolored crystal indicated a purity higher than that of a typical Harshaw crystal. The second crystal investigated was grown in the author's apparatus from doubly recrystallized potassium chloride, and is designated B.

Production of the N₁ Band

It was found that a prominent N₁ band could be produced by first bleaching a colored crystal with F light and then giving the crystal a heat treatment. F-light bleaching was carried out until the spectrum of the crystal showed the M band to be somewhat smaller than the R bands. The bleached crystal was wrapped in aluminum foil and placed in a drying oven for 15 minutes at a temperature of about 90°C. This treatment resulted in the destruction of the R bands and the growth of the N₁ band. After heating, the foil-wrapped crystal was quickly brought to room temperature by waving it in the air.

Two examples of this method of producing the N₁ band are given. Figure 24 involves a colored portion of crystal A having an
Fig. 24.—Thermal production of the $N_1$ band

The spectrum at 80$^\circ$K of additively colored KCl ($n_e = 4.4 \times 10^{16}$ cm$^{-3}$) is shown (a) following 2½ hr treatment of F-light irradiation at room temperature, prior to thermal treatment and (b) following 15 min at 90$^\circ$C. Note change in absorbance scale above 0.85 absorbance units.
initial F-center concentration \( n_F^0 \), assuming unit oscillator strength, of \( 4.4 \times 10^{16} \text{ cm}^{-3} \); this portion is designated \( A_1 \). The curves in the figure show that the R and \( N_2 \) bands were reduced as a result of heating the crystal, while the \( F \), \( M \) and \( N_1 \) bands were enhanced. Tomiki (77, p. 490) did not observe the thermal destruction of the \( N_2 \) band because the spectrophotometer used in his experiments had an upper wavelength limit of 1000 m\( \mu \).

A more prominent \( N_1 \) band is exhibited in Figure 25, which shows the effect of heating a more intensely colored portion of crystal A (given the notation \( A_2 \)) after F-light bleaching. The initial F-center concentration in this case was \( 1.8 \times 10^{17} \text{ cm}^{-3} \).

\[ N_1 \text{-Light Bleaching} \]

Following growth of the \( N_1 \) band, the effect of \( N_1 \)-light irradiation on this band was determined. Figure 26 shows the changes in the spectrum of crystal \( A_1 \) resulting from successive irradiations; the initial spectrum (a) is identical to curve (b) of Figure 24. Crystal \( A_2 \), however, was given additional heat treatments of five minutes each at 96 and 100\( ^\circ \text{C} \) before bleaching with \( N_1 \) light. The spectrum recorded prior to bleaching and after each bleaching period is shown in Figure 27. It is evident that the \( N_1 \) band is unstable to \( N_1 \) light; the irradiation also leads to a
Fig. 25.- Thermal production of the $N_1$ band

The spectrum (at 80°K) of additively colored KCl ($n^2=1.8 \times 10^{17}$ cm$^{-3}$) is shown (a) following 8 hr of $F$-light irradiation at room temperature, prior to heat treatment and (b) after 15 min at 90° C.
Fig. 26.- N₁-light bleaching of additively colored KCl

The spectrum (at 80° K) of a crystal with \( n_0^2 = 4.4 \times 10^{16} \) cm\(^{-3} \) is shown following thermal production of the N₁ band and (a) 0 (b) 25 (c) 125 (d) 10\(^3\) min of total N₁-light (1000 m\( \mu \)) bleaching at room temperature.
Fig. 27 - N₁-light bleaching of additively colored KCl

The spectrum, measured at 80⁰K, of a crystal initially containing 1.8 x 10¹⁷ F centers/cm³ is shown following thermal production of the N₁ band and (a) 0 (b) 20 (c) 60 (d) 120 (e) 300 min total N₁-light bleaching at room temperature.
reduction in the F and M bands, while the N\textsubscript{2} and R bands are increased.

Effect of F-light Bleaching on the N\textsubscript{1} Band

If a crystal is bleached with F light until the N bands have achieved some prominence, and is then allowed to stand in the dark, only slight changes occur in the R and N\textsubscript{2} bands upon standing. However, definite increases can be observed in the N\textsubscript{1} and M bands. If the crystal is again-irradiated with F light, the N\textsubscript{1} band decreases and the N\textsubscript{2} band increases, as was observed by Herman, Wallis and Wallis (31). These effects are illustrated in Figure 28, involving crystal A\textsubscript{2}. Possible changes in the F band were not observed; the F-center concentration of the crystal was too high to permit optical measurement.

N\textsubscript{2}-Light Bleaching

The N\textsubscript{2} center is unstable to N\textsubscript{2} light, as shown in Figure 29. The initial F-center concentration of crystal B was 1.4 x 10\textsuperscript{17} cm\textsuperscript{-3}. The effect of N\textsubscript{2}-light irradiation following bleaching with F light was to decrease the N\textsubscript{2} and R bands, and to increase the N\textsubscript{1} and F bands. In this particular case the M band was unchanged, but in experiments with another crystal, the M band
Fig. 28.- The effect of F-light bleaching on the $N_1$ band

The spectrum at 80°K of additively colored KCl ($n_F = 1.8 \times 10^{17} \text{cm}^{-3}$) is shown following (a) 225 min of F-light (550 m$\mu$) bleaching at room temperature, (b) overnight storage in the dark, and (c) an additional 270 min of F-light bleaching.
Fig. 29. - N₂-light bleaching of additively colored KCl

The spectrum (measured at 80°K) of a crystal with n₂=1.4 x 10¹⁷ cm⁻³ is shown following (a) extended F-light bleaching and (b) 2 hr of N₂-light bleaching at room temperature. (λ 1070 mμ)
grew under similar conditions. The constancy observed in crystal B was probably fortuitous.

Behavior of the Thermally Enhanced N Band on Storage

Crystal B was subjected to a 15-minute heat treatment at 90°C to enhance the N band, and was then allowed to stand in place overnight. Figure 30 shows that the N and R bands grew at the expense of the N band while the crystal stood in the dark. The M band remained unchanged.

Discussion

Model Assignment and Color Center Reaction Mechanisms

In order to account for the color center reactions involving the N bands, it is necessary to postulate models for the various centers and corresponding mechanisms for the reactions. If reasonable mechanisms can account for each of the color center reactions, the model assignments are accorded considerable support.

Suggested models for the various centers to be discussed are illustrated in Figure 31.

F Center. There is sufficient reason for accepting the F
Fig. 30.- Thermal decrease of the $N_i$ band

The spectrum, at 80°K, of additively colored KCl ($n_o = 1.4 \times 10^{17} \text{ cm}^{-3}$) is shown following (a) thermal production of the $N_i$ band and (b) overnight storage in the dark.
Fig. 31. - Suggested color center models

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+ - + - +
- + + - -
+ - + - +
- + - + -

F center - an electron trapped at a negative ion vacancy

M center (Pick)

R center (Pick)

N₂ center

[[110]]

N₁ center

N₃ center
center as an electron trapped at a negative ion vacancy that the validity of this model is no longer discussed. The reasons for its adoption are summarized by Kittel (40, p. 493-494).

**M Center.** There has been considerable debate as to whether the M band should be attributed to a one- or a two-electron center. The one-electron center proposed by Seitz (69, p. 404-405) is that of an F center associated with a vacancy pair; two cation sites, one occupied and the other vacant, are adjacent to the two negative ion vacancies. To account for the inversion symmetry of the center, Knox (41) suggested that the adjacent cation be shifted to a position midway between the two cation sites. The center thus modified may be described as an alkali metal atom in a planar vacancy quartet.

Pick, however, has suggested that the M center may be simply two associated F centers (60). Recent evidence (20) seems to favor this assignment. Perhaps the most convincing evidence is the apparent diamagnetism of the center (57).

**R Center.** As a model for the R center, Pick proposed a planar association of three F centers (60). He calculated the degree of polarization of fluorescence on the basis of this assignment, and found excellent agreement with experiment. The fact that the rate of R-center formation is proportional to M-center
concentration (9; 59, p. 451-452) appears to support Pick's suggestion.

**Transport of Negative Ion Vacancies.** The formation of complex centers from the F center requires the transport of negative ion vacancies. Assuming a uniform distribution of F centers, and making further reasonable assumptions as to the magnitude of the parameters involved, Seitz (69, p. 406) estimated the upper limit for the activation energy of the transport process to be about 0.5 ev. Since this was much lower than the activation energy for the diffusion of the negative ion vacancy as determined by ionic conductivity measurements, about 1 ev, it was suggested that the mobile species was the neutral vacancy pair. When this suggestion found support in the work of Dienes (14, p. 632), who calculated the activation energy for diffusion of the vacancy pair to be 0.375 ev, it became generally accepted that negative ion vacancies were transported via mobile vacancy pairs.

However, recent recalculation of the activation energy for diffusion of the vacancy pair by Tharmalingam and Lidiard (76) indicates that it is at least comparable to that of the negative ion vacancy and is probably greater. The value reported by them is 1.30 ev. This exceeds the activation energy for diffusion of the negative ion vacancy in potassium chloride, 1.18 ev as calculated
by Guccione, Tosi and Asdente (24). This turn of events calls into serious question the assumption of uniform distribution of F centers, and strongly supports the suggestion of Mitchell (49, p. 498) that color centers are localized near dislocations.

Delbecq, Pringsheim and Yuster (12) found that bleaching a colored crystal with F light at low temperatures gives rise to a band near the ultraviolet absorption edge of potassium chloride. They associated the band with the negative ion vacancy, and gave it the name alpha. The band does not appear when bleaching takes place at room temperature; for an explanation of this behavior it was suggested that isolated vacancies are destroyed by the formation of mobile pairs. Direct migration of the negative ion vacancy now appears more likely.

Recent experiments by Itoh and Suita (36) involving bleaching with pulsed F light demonstrate the formation of complex centers from the newly formed negative ion vacancies, and show that the process is diffusion limited with an activation energy of 0.95 ± 0.2 ev.

The Triangular Diffusion Mechanism. When a crystal containing M centers is irradiated with M light polarized in a [110] direction, those M centers whose axes are similarly directed absorb more strongly than those whose axes are not parallel to the
direction of polarization of the bleaching light. Therefore, the M centers with axes aligned in a [110] direction are depleted more rapidly than the others, and the distribution of orientation of the M centers in the crystal is not uniform. This leads to optical anisotropy of the crystal, or dichroism. The dichroism thus induced in potassium chloride crystals containing M centers decays slowly at room temperature, and is still detectable after 20 to 30 hours (37). However, the decay becomes rapid when the temperature is raised to 50 or 60°C, as was observed by Tomiki (77, p. 493 & 499). By studying the rate of decay of dichroism Tomiki found the activation energy for the thermal reorientation of the M center to be 1.0 ev (78)

A mechanism called the triangular diffusion mechanism is postulated for reorientation of the M center. The two F centers constituting the M center, and a negative ion which is next-nearest neighbor to both, form an equilateral triangle in a (111) plane as illustrated in Figure 32. Reorientation of the M center is accomplished if the chloride ion and either of the two M-center electrons are interchanged. To obtain an idea of the magnitude of the activation energy for this process, comparison is made to the activation energy for diffusion of a negative ion vacancy.

Diffusion of a chloride ion to the point midway between two anion sites is favored by the effective positive charge of the
Fig. 32. Triangular diffusion mechanism for the M center

(a) The two F centers comprising the M center form an equilateral triangle in a (111) plane with a chloride ion which is next-nearest neighbor to both F centers. The chloride ion begins to move along an edge of the triangle. (b) Migration of the chloride ion and accompanying redistribution of M-center electrons have been completed. The M center is reoriented.
adjacent negative ion vacancy. If the M-center electrons were to maintain their positions as a chloride ion moved to the saddle point, the energy of the process would be considerably greater than the activation energy for diffusion of the negative ion vacancy. However, the M-center electrons do not maintain their positions. Not only do they begin to move out of the vacancy toward which the chloride ion is moving, giving it a partial positive charge, but they also move in behind the chloride ion and reduce the effective positive charge of the newly formed vacancy. These factors may lower the activation energy for the triangular diffusion mechanism enough to make it comparable in magnitude to that for diffusion of a negative ion vacancy, though the rate of decay of dichroism would indicate it to be somewhat larger.

The triangular diffusion mechanism need not be limited to reorientation of the M center. A similar process may lead to rearrangement or diffusion of more complex centers. The mechanism may be applied to the $F^+_2$ center (two associated F centers with one electron missing) which was postulated by Seitz (69, p. 404-405) as the center responsible for the R1 band. While the existence of the $F^+_2$ center as a stable center in potassium chloride has not been demonstrated, it has at least a transient existence as a precursor of the M center.
The activation energy for diffusion of the $F^+_2$ center should be lower than that for diffusion of the M center. Because of the effective positive charge of the $F^+_2$ center, the potassium ions strained by the diffusing chloride ion are moved outward more easily than are the corresponding ions during reorientation of the M center. It is suggested that the $F^+_2$ center may be of considerable importance in the formation of R and N centers.

$N_1$ Center. As mentioned previously, the model proposed by Pick for the $N_1$ center is a planar association of four $F$ centers. Assuming that each of the four electrons behaves almost independently, and that wave-function overlap expresses itself in a change in transition moment, he predicted that the center would have additional absorptions under the $F$ and $R$ bands. However, Okamoto (58) has found that polarized 1000-mµ light produces anisotropic absorptions correlating the $N_2$ rather than the $N_1$ band with $F$- and $R$-band absorptions. Hence the model assigned by Pick to the $N_1$ center is rejected.

The dichroism induced in the $N_1$ band by polarized light indicates that the absorbing dipole responsible for the $N_1$ band is oriented in the [110] direction (58). Since Pick's model for the $N_2$ center, a tetrahedral association of four centers, has symmetry such that it cannot exhibit dichroism, neither of his suggested
models for the N centers can account for the properties of the $N_1$ center.

A linear association of three $F$ centers which would have no R-band absorption is postulated as a model for the $N_1$ center. Following the reasoning of Pick, the two outer electron clouds would overlap the inner electron clouds in a manner identical to that in the M center, and would lead to M and F absorptions. With a double overlap, the inner electron would have its transition moment in a $[110]$ direction reduced below that of the other two. It would absorb light of energy lower than that of the M band, and the optical dipole for this absorption is seen to be along a $[110]$ direction as required.

The existence of the center derived from association of four $F$ centers along a face diagonal is also proposed. The optical properties of this center, called the $N_3$ center, would be essentially those of the $N_1$ center. The outer two $F$ centers would have $F$- and $M$-type absorptions, and the inner two would have $F$- and $N_1$-type absorptions.

$N_2$ Center. Bron (5) has reported that the $N_2$ absorption band always varies in magnitude in direct proportion to the variations in the R bands, and has suggested that the $N_2$ band may arise from an absorption of the R center. Hattori (28) found the rates of growth of the R and $N_2$ bands to be proportional; the constant of
proportionality, however, differs markedly for different crystals. In addition, Moran and coworkers (51) have reported a fivefold thermal decrease in the R bands accompanied by an only threefold decrease in the N₂ band. It is concluded that the N₂ band does not arise from the R center.

It would appear that the N₂ center must contain the R center as a structural element if it is to have R-band absorptions. The R center contained in the N₂ center cannot be greatly perturbed because the R bands of the two centers coincide.

Okamoto found that 1000-mµ light produced dichroism in the M band, but did not find that it was correlated with the dichroism of the N₁ band. The lack of correlation could be explained if the N₂ band also had an absorption under the M band. The simplest center having secondary absorptions under F, M and R bands would be obtained by association of a fourth F center with an R center in such a manner that three of the F centers are aligned in a [100] direction. Hence this model is assigned to the N₂ center.

Hattori (28) observed that irradiation with M light following extended F-light bleaching enhances the N₁ band at the expense of the N₂ band, while the reverse behavior occurs when the N₁ band has been thermally enhanced. This supports the view that both N centers have M-band absorptions.
Summary of color center absorptions. The positions of the characteristic absorption of each of the color centers at $77^\circ$K, and the types of secondary absorptions predicted for each by the theory of Pick, are given in the following table.

Table 4. Absorptions of the color centers

<table>
<thead>
<tr>
<th>Center</th>
<th>Wavelength of characteristic absorption, $\mu\text{m}$</th>
<th>Type of secondary absorption</th>
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<tr>
<td>F</td>
<td>538</td>
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<tr>
<td>M</td>
<td>801</td>
<td>F</td>
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<tr>
<td>R</td>
<td>658, 730</td>
<td>F</td>
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<tr>
<td>$N_1$, $N_3$</td>
<td>964</td>
<td>$M$, $F$</td>
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<tr>
<td>$N_2$</td>
<td>1020</td>
<td>$M$, $R$, $F$</td>
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Explanation of Experimental Results

Thermal Destruction of the R and $N_2$ Bands. The enhancement of the $N_1$ band occurring at the expense of the $N_2$ and R bands upon storage of partially bleached potassium chloride in the dark at room temperature (Figure 28), as well as its enhancement resulting from heat treatment, is viewed as arising from rearrangement of the R and $N_2$ centers to the corresponding linear centers by the triangular diffusion mechanism. The reverse of this process would account for the decrease in the thermally enhanced $N_1$ band on storage if it
were not for the observed constancy of the M band (Figure 30). Conversion of $N_1$ centers to R centers, and of $N_3$ centers to $N_2$ centers, should both cause a decrease in the M band. As only one observation of this constancy was made, and as it is the only result which cannot be explained in terms of the assumed models, this behavior should be reinvestigated. A slight frosting of the windows of the Dewar vessel could have raised the background absorption and led to the apparent constancy of the M band.

Optical Destruction of the $N_1$ Band. Hattori (28) has studied the optical destruction of the thermally enhanced $N_1$ band more thoroughly than has the author. In addition to the decrement produced in the band by F and $N_1$ light, he reported that it is also decreased by M light and by light of the wavelengths 490 and 720 mµ. He observed that the ratio of the change in the $R_2$ band to the change in the $N_1$ band remains constant during irradiation with each type of light, but that the ratio is different for each type and decreases in the order F, 490 mµ, M, 720 mµ and $N_1$. The ratio of the changes in the $R_2$ and $N_1$ bands accompanying F-light irradiation and the ratio observed during thermal enhancement of the $N_1$ band are the same, indicating that $N_1$ and $N_3$ centers are converted to R and $N_2$ centers without dissociation, rearrangement alone being involved. The other ratios indicate that rearrangement is accompanied in part
by disassociation of a negative ion vacancy or other structural element from the $N_1$ and $N_3$ centers. For example, there may be some conversion of $N_1$ centers to $M$ centers and $F$ centers rather than to $R$ centers.

The dissociation of the $N_1$ and $N_3$ centers by $N_1$ light may occur in a manner which leaves the remaining two or three centers undisturbed. This may account for a fact which would otherwise cast some doubt on the model assignments for the $N_1$ and $N_3$ centers. The ratio of the $M$ band to the $N_1$ band in a dichroic spectrum obtained by irradiation with $N_1$ light polarized in a [100] direction is 1 to 5, according to Okamoto. It would seem that the $M$, $N_1$ and $N_3$ centers should all have similar oscillator strengths for $M$-type absorption, as each contains two $F$ centers which absorb $M$ light. If this is true, the $M$ and $N_1$ bands in the dichroic spectrum should be of similar magnitude. However, if an $N_1$ center is destroyed in a manner which leaves an $M$ center oriented in the same direction as the original $N_1$ center, no marked change in the $M$ band is to be expected. It is also to be noted that rearrangement of the $N_3$ center to the $N_2$ center is most likely to occur without reorientation of that portion of the $N_3$ center which gives rise to the $M$ band following the rearrangement. Therefore, an $M$-to-$N_1$ band ratio of 1:5 is not inconsistent with the postulated models.

The destruction of the $N_1$ band by 720-ms light requires special comment, since Hattori views this destruction as evidence for an
R-type absorption for the $N_1$ center. He has divided the thermally induced color center reactions into two stages: a first stage during which the $N_1$ band grows rapidly as a result of destruction of the R and $N_2$ centers, and a slow second stage in which the $N_1$ band and the much-reduced R bands decay together. Hattori feels that these reduced R bands are due to the $N_1$ center, while the author feels that they arise from R and $N_2$ centers which are present in thermal equilibrium with $N_1$ and $N_3$ centers. A dichroic spectrum included in the paper by Okamoto (58) shows a weak band lying between the R bands, which may be associated with the $N_1$ band. This band, possibly due to a higher-order transition of the $N_1$ center, could account for the optical destruction of the $N_1$ band by 720-mÅ light.

Optical Destruction of the $N_2$ Band. Rearrangement of the $N_2$ center to the $N_3$ center by irradiation with $N_2$ light cannot alone account for the spectral changes shown in Figure 29. Enhancement of the $N_1$ band and decrease of the R bands occur as expected, but growth of the M band would also be expected if rearrangement were the sole effect of the $N_2$-light irradiation on the $N_2$ center. This may be seen from the fact that two of the F centers in the postulated $N_3$ center have absorption modes in the M-band region, while there is only one such F center in the $N_2$ center. Indeed, as noted earlier, growth of the M band took place in another crystal treated similarly.
Constancy of the band, however, can be explained if ionization of the N₂ center is followed by disassociation of a negative ion vacancy and subsequent association of this vacancy with an M center to form an R center.

Summary

On the basis of the assumed models and mechanisms, it has been possible to present a consistent qualitative explanation of a number of color center reactions. The models used are consistent with the dichroic properties of the absorption bands, as well as with the variations produced by thermal and optical treatment, and are also in accord with the theoretical considerations of Pick. Color centers are viewed as being localized near dislocations. Transport of negative ion vacancies may occur as a result of diffusion of the F⁺₂ center as well as by direct migration. Rearrangement of color centers and diffusion of the F⁺₂ center are thought to occur by the triangular diffusion mechanism. Enough experimental information is consistently correlated to give considerable support to both models and mechanisms. The various observations and the suggested color center reactions are summarized in Table 5.
Table 5. Color center observations and reactions

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<th>Treatment of crystal</th>
<th>Effect on band intensity</th>
<th>Reaction</th>
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<td>F-light bleaching following extended F-light bleaching and room-temperature annealing</td>
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<td>N₂-light irradiation following extended F-light bleaching</td>
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<td>Room-temperature annealing following extended F-light bleaching</td>
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<td>Annealing at 95°C following extended F-light bleaching</td>
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<td>As above followed by room-temperature annealing</td>
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D = decrease  I = increase  S = slight effect  e⁻ = electron
□ = negative ion vacancy
The Color Center Behavior of KCl(K$_2$SO$_4$)

General

Potassium chloride crystals containing potassium sulfate were colored additively and their absorption spectra were investigated in the regions 250-2000 mµ and 650-4000 cm$^{-1}$. The color center behavior of these crystals was found to differ markedly from those not containing potassium sulfate. Tentative model assignments are discussed for some of the new absorption bands, and evidence is presented for the reduction of the sulfate ion during additive coloration.

Experimental

Preparation of Crystals

Each of the sulfate-doped crystals used in this study was grown under nitrogen in the author's apparatus from a melt containing 2 mg of potassium sulfate per gram of potassium chloride, with a stirring rate of 90 rpm. The sulfate ion concentration of a portion of one of the crystals, designated C, was calculated from the distribution coefficient to be $1.5 \times 10^{16}$ cm$^{-3}$, while that of a piece of a second crystal, D, was determined by tracer analysis of an adjacent portion to be $1.9 \times 10^{16}$ cm$^{-3}$. Crystal C was additively colored to an F-center concentration of $7.5 \times 10^{15}$ cm$^{-3}$, and crystal D to an F-center concentration of $4.9 \times 10^{16}$ cm$^{-3}$. Note that in crystal D the density
of F centers exceeds that of sulfate ions prior to coloration, and that in crystal C the converse is true. The pure potassium chloride crystal A (grown by Gruzensky) has been used for purposes of comparison.

**Reduction of the Sulfate Ion**

It was found that the sulfate ion is not stable in potassium chloride under the conditions of additive coloration. The infrared spectrum of a KCl(K₂SO₄) crystal before and after coloration was observed in the sodium chloride region using a Perkin-Elmer model 20 infrared spectrophotometer. The concentration of sulfate ion in the instrument path was calculated to be 0.15 µM/cm². Disappearance of the absorption in the asymmetric stretching region of the sulfate ion, as shown in Figure 33, indicates the absence of sulfate ion in the crystal subsequent to additive coloration. A new peak, however, appeared at 875 cm⁻¹, and remained after the crystal was returned to a coloring capsule and subjected to potassium vapor at 600°C for one week. No other absorptions were observed between 650 and 4000 cm⁻¹.

Further evidence for reduction of the sulfate ion was obtained by the precipitation of radioactive silver sulfide from a solution in which was dissolved a piece of colored crystal grown from a melt
Fig. 33. – The effect of additive coloration on the infrared absorption spectrum of \( \text{KCl}(\text{K}_2\text{SO}_4) \).

The spectrum of a crystal grown from a melt containing 1.9 mg \( \text{K}_2\text{SO}_4 \) per g KCl is shown (a) before and (b) after coloration.
containing radioactive sulfate. The crystal portion was dissolved in ammonium hydroxide; sodium sulfide and silver nitrate were added, and the silver chloride was dissolved in ammonium hydroxide following a two-hour digestion period. The silver sulfide formed was found to have retained 57 percent of the total activity of the crystal, when the self-absorption coefficient of silver sulfide was assumed to be identical to that of barium sulfate. Because this observation was limited to a single experiment involving only a small piece of colored crystal D, the numerical result is unreliable, but reduction of the sulfate ion is clearly demonstrated. Adsorption of radioactive sulfate ion on the silver sulfide could not have accounted for the observed activity.

The Absorption Spectrum of $\text{KCl(}K_2\text{SO}_4\text{)}$

The reduction products of the sulfate ion greatly affect the color center behavior of potassium chloride. The effect of F-light bleaching on the spectrum of crystal C, and its effect on the spectra of two portions of crystal D are shown in Figures 34, 35 and 36. For purposes of comparison, the positions of bands observed in undoped potassium chloride are indicated in Figures 34 and 35. All spectra were measured at liquid nitrogen temperature, and absorbance was set equal to 2000 m\(\mu\).
Fig. 34: F-light bleaching of additively colored KCl (K₂SO₄)

The spectrum (at 80°K) of a KCl crystal having an initial F-center concentration of 7.5 x 10¹⁵ cm⁻³ and a sulfate ion concentration of 1.5 x 10¹⁶ cm⁻³ is shown after the following total times of F-light bleaching at room temperature: (a) 0, (b) 3 1/2, (c) 17 min.
Fig. 35.- F-light bleaching of additively colored KCl(K₂SO₄)

The spectrum at 80°K of a KCl crystal having an initial F-center concentration of 4.9 x 10¹⁶ cm⁻³ and a sulfate ion concentration of 1.9 x 10¹⁶ cm⁻³ is shown following (a) 0, (b) 1, (c) 3, (d) 9, and (e) 20 min total bleaching with F-light at room temperature.
Fig. 36. F-light bleaching of additively colored KCl(K$_2$SO$_4$)

The spectrum (at 80°K) of a KCl crystal having an initial F-center concentration of 4.9 x 10$^{16}$/cm$^3$ and a sulfate ion concentration of 1.9 x 10$^{14}$/cm$^3$ is shown following (a) 0 (b) 20 (c) 100 and (d) 780 min total F-light bleaching at room temperature.
Rate of F-light Bleaching. The rate of bleaching of the F band was found to be much greater in crystals doped with potassium sulfate than in undoped crystals. A one-minute F-light irradiation of crystal D (Figure 35) reduced the F band by 14 percent, while only a 3 percent reduction in the F band resulted from a one-minute irradiation of the pure crystal A of similar F-center density. Though the F band was not in any case completely annihilated by bleaching a sulfate-doped crystal, it was bleached to a much greater extent than was possible in the pure crystals.

New Absorption Bands. Two new absorption bands appeared in the spectra of both crystals C and D prior to bleaching. The $S_2$ band, at 364 m$\mu$, is most prominent in Figure 34. This band decreases with F-light bleaching, but the decrease is generally obscured by a general increase in absorption in the region extending from the F band into the ultraviolet. The small band distorting the M band has its peak at approximately 815 m$\mu$ and is called the $S_3$ band. Both M and $S_3$ bands, as well as bands on the long wavelength side of these absorptions, were observed to grow with F-light bleaching.

Only very small R bands can be seen in the spectra of crystal D (Figures 35 and 36) and these bands are absent in the spectrum of crystal C (Figure 34) in which the concentration of F centers prior
to bleaching was exceeded by that of sulfate ions prior to coloration.

The absorbance in the region to the long wavelength side of the $S_3$ band evidently involves several bands, some appearing rapidly and others appearing only after extended F-light bleaching. The narrowest of these bands, which resulted from extended bleaching and is located at about 870 mµ, is called the $S_4$ band. It is seen to best advantage in Figure 36 (d). None of the absorbance in the 1000-mµ region in Figure 34, and only a small part of the absorbance in that region in Figures 35 and 36, can be attributed to the presence of $N_2$ centers, because the presence of these centers requires R-band absorptions.

The growth of absorption in the 1000-mµ region as F-light bleaching was begun, and the decrease of this absorption following extended bleaching, seem to be associated with a general rise and fall in absorbance in the ultraviolet region upon bleaching, as shown in Figure 37.

**Effect of Heat Treatment.** Following F-light bleaching, crystal C was wrapped in aluminum foil and given heat treatments at various temperatures in a drying oven. After each treatment the crystal was returned to the Dewar cell in the spectrophotometer in the dark and its spectrum was observed at liquid nitrogen temperature. The results are shown in Figure 38. The heat treatment at
Fig. 37.—The effect of F-light bleaching on the ultraviolet spectrum of additively colored KCl(K₂SO₄)
The spectrum, measured at 80°K, of a KCl crystal initially containing 4.9 x 10¹⁶ F centers/cm³ and 1.9 x 10¹⁶ sulfate ions/cm³ is shown following (a) 0 (b) 10 and (c) 100 min total F-light bleaching at room temperature.
Fig. 38.—The effect of thermal treatment on additively colored \( \text{KCl(K}_2\text{SO}_4) \) following F-light bleaching

The spectrum (at \( 80^\circ\text{K} \)) of a crystal initially containing \( 7.5 \times 10^{15} \) F centers/cm\(^3\) and \( 1.5 \times 10^{16} \) sulfate ions/cm\(^3\) is shown after the following successive treatments: (a) 2 hr of F-light bleaching at room temperature (b) 10 min heat treatment at \( 102^\circ\text{C} \) and 10 min at \( 111^\circ\text{C} \) (c) 10 min at \( 120^\circ\text{C} \) (d) 30 min at \( 126^\circ\text{C} \) and (e) 40 min at \( 150^\circ\text{C} \).
126°C, curve (d), annihilated the $S_2$ band though it did not destroy the broader absorption underneath. The $S_3$ band was the only prominent band remaining on the long wavelength side of the F band after that treatment, and even the $S_3$ band was obliterated by the 150°C treatment, curve (e). It should be pointed out that curves (d) and (e) were arbitrarily lowered to obtain a truer comparison with the other curves, because apparent fogging of the crystal surface during these two heat treatments caused an exaggeration of the absorbance.

Figure 39 shows the changes in the ultraviolet region of the spectrum attending the heat treatments of crystal C. A sharp band at 284 mµ, designated the $S_1$ band, was greatly enhanced by the heat treatment at 150°C but was present in the spectrum even prior to F-light bleaching. An ultraviolet spectrum of pure potassium chloride colored to a similar F-center density has been included in the figure.

Discussion

Stability of a Divalent Anion in KCl under Conditions of Coloration

The original intent in doping potassium chloride with potassium sulfate was to introduce a stoichiometric excess of negative ion vacancies into the crystal. Because of reduction of the sulfate
Fig. 39.—Thermal production of the $S_1$ band

The ultraviolet spectrum of an additively colored KCl(K$_2$SO$_4$) crystal initially containing $1.5 \times 10^{16}$ sulfate ions and $7.5 \times 10^{16}$ F$^-$ centers/cm$^3$ is shown following (a) 1 min F-light bleaching at room temperature (b) 2 hr F-light bleaching plus a 30 min heat treatment at $126^\circ$C, and (c) 40 min heat treatment at $150^\circ$C. For comparison, a curve (d) is included for pure KCl, additively colored but unbleached and containing $4.4 \times 10^{16}$ F centers/cm$^3$. 
ion, as evidenced by the disappearance of absorption in the asymmetric stretching region of the sulfate ion following additive coloration, it is not apparent that this objective was achieved.

Let $X^{--}$ represent a possible divalent anion resulting from reduction of the sulfate ion. The stability of $X^{--}_{(c)}$ (that is, $X^{--}$ present in the crystal) with respect to formation of $X^-_{(c)}$ under the conditions of additive coloration depends on the extent to which this reaction proceeds

$$X^{--}_{(c)} + \text{negative ion vacancy} \rightarrow X^-_{(c)} + \text{F center}.$$ 

The energy of this reaction, $\Delta E$, is evaluated by considering the reaction to take place in the following steps:

1. Removal of an electron from the divalent anion to form a univalent ion and a gaseous electron; $X^{--}_{(c)} \rightarrow X^-_{(c)} + e^-_{(g)}$.

2. Removal of a potassium ion from the crystal to form a positive ion vacancy and a gaseous potassium ion; $K^+_{(c)} \rightarrow K^+_{(g)} + \text{positive ion vacancy}$.

3. Annihilation of a negative ion vacancy and a positive ion vacancy by migration to the crystal surface.

4. Reaction of a gaseous potassium ion and an electron to form a potassium atom; $K^+_{(g)} + e^-_{(g)} \rightarrow K_{(g)}$.

5. Formation of a crystalline potassium ion and an F center.
from a potassium atom; $K(g) \rightarrow K^+(c) + F$ center.

The energy of step (1) involves three terms: $EA$, the affinity of the ion $X^-$ for an electron; $E_L$, the lattice energy; and $P_-$, the polarization energy of the crystal which is associated with the divalent anion. The contribution of the divalent anion to the lattice energy of the crystal is not precisely twice that of the monovalent ion, because of factors such as the variation in the repulsive potential resulting from the difference in size of the two ions. However, the lattice energy of potassium chloride, given by Kittel (40, p. 80) as 7.2 ev, still approximates well the change occurring in the repulsive and coulombic potentials of the crystal when a univalent anion is exchanged for a divalent anion. The divalent anion polarizes the surrounding crystal. The polarization energy for introduction of unit charge in potassium chloride, from Mott and Littleton (53, p. 497), is 2.39 ev. Though this calculation is usually applied to the polarization associated with a negative ion vacancy, it is equally applicable to the present case, the only difference being the direction of the polarization vectors.

The removal of the potassium ion from the crystal, step (2), will require an amount of energy equal to the lattice energy less the polarization energy $P_+$ associated with the positive ion vacancy, which is 2.71 ev (53, p. 497). The annihilation of a positive and
negative ion vacancy by diffusion to the crystal surface, step (3), lowers the energy of the crystal by an amount equal to the formation energy of the two isolated vacancies, $\phi_s = 2.0$ ev (15). Reaction of the gaseous potassium ion and electron in step (4) releases an amount of energy, I, equal to the ionization potential, or 4.4 ev. Finally the energy of formation of an F center from potassium vapor involved in step (5) has been given by Dekker (11, p. 379) as $\phi_F = -0.01$ ev.

In summary, the reaction energies for the five steps are

(1) $E_L + EA + P_- = 7.2 + EA + 2.4$ ev

(2) $E_L - P_+ = 7.2 - 2.7$ ev

(3) $-\phi_s = -2.0$ ev

(4) $-I = -4.4$ ev

(5) $\phi_F = -0.1$ ev,

from which the energy change for the overall reaction is

$$\Delta E = 2 E_L + EA + P_+ - P_- - \phi_s - I + \phi_F = EA + 7.6$$ ev.

Neglecting the small numerical difference between energy and enthalpy, as well as changes in the vibrational spectrum of the crystal arising as a result of the reaction, one finds that the equilibrium constant of the reaction is given by

$$\frac{n_F n_X^-}{n_v n_X^{--}} = \exp \left( -\frac{\Delta E}{kT} \right)$$
where \( n_F \) is the number of \( F \) centers, \( n_X^- \) the number of univalent anions \( X^- \), \( n_v \) the number of negative ion vacancies and \( n_{X^{2-}} \) the number of divalent anions \( X^{2-} \) in the crystal.

The concentration of color centers in the colored crystals is of the same order as that of the sulfate ion prior to coloration, so it is apparent that if the reaction is very exoergic, that is, if the electron affinity of \( X^- \) is much less than -7 or -8 ev, the element \( X \) will be unstable as a divalent anion in potassium chloride under the conditions of additive coloration. Pertinent electron affinity data are collected in Table 6.

### Table 6. Electron affinities for species of sulfur and oxygen

<table>
<thead>
<tr>
<th>Species</th>
<th>First EA, ev</th>
<th>Double EA, ev</th>
<th>Second EA, ev</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>3.45</td>
<td></td>
<td></td>
<td>(10)</td>
</tr>
<tr>
<td>S</td>
<td>( \text{EA}_{\text{Br}} -1.23 = 2.32 )</td>
<td>-3.9 ± 0.4</td>
<td>-6.2 ± 0.4</td>
<td>(2; 4, p. 745)</td>
</tr>
<tr>
<td>O</td>
<td>1.46</td>
<td>-6.15 ± 0.08</td>
<td>-7.6</td>
<td>(79; 4, p. 745)</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>0.73</td>
<td>-5.12</td>
<td>-5.95</td>
<td>(38)</td>
</tr>
<tr>
<td>( \text{SO} )</td>
<td>( \text{EA}_O -0.45 ± 0.1 = 1.0 )</td>
<td></td>
<td></td>
<td>(55)</td>
</tr>
</tbody>
</table>

The Chemical Species of Oxygen Resulting from Reduction of \( \text{SO}^{4-} \)

Of the several species of oxygen which might be present in the doped potassium chloride following reduction of the sulfate ion, peroxide turns out to be the one which is stable. This is
demonstrated by showing that the reactions

(A) \( \text{O}_2^{--} + \text{negative ion vacancy} \rightarrow \text{O}_2^- + \text{F center} \)

(B) \( \text{O}_2^{--} + \text{negative ion vacancy} \rightarrow 2 \text{O}^- \)

(C) \( \text{O}_2^{--} + 2 \text{F centers} \rightarrow 2\text{O}^{--} + \text{negative ion vacancy} \)

do not occur to any appreciable extent.

The energy of reaction (A) is equal to 7.6 ev plus the electron affinity of superoxide ion, -5.95 ev; the sum is 1.6 ev. The reaction is sufficiently endoergic to preclude the possibility of any appreciable oxidation of peroxide ion to superoxide ion.

Consider the reaction (B) to take place in the following steps:

(1) Removal of a peroxide ion from the crystal to give the gaseous ion and a negative ion vacancy;

\[ \text{O}_2^{--} \rightarrow \text{O}_2^{--} + \text{negative ion vacancy} \]

(2) Dissociation of two electrons from the gaseous peroxide ion to give an oxygen molecule and two free electrons;

\[ \text{O}_2^{--} \rightarrow \text{O}_2^{--} + 2\text{e}^- \]

(3) Dissociation of the oxygen molecule to give two oxygen atoms;

\[ \text{O}_2^{--} \rightarrow 2\text{O}^- \]

(4) Association of a free electron with each of the two oxygen atoms;

\[ 2\text{O}^- + 2\text{e}^- \rightarrow 2\text{O}^{--} \]

(5) Incorporation of the singly charged oxygen ions into the crystal;

\[ 2\text{O}^{--} + 2 \text{negative ion vacancies} \rightarrow 2\text{O}^{--} \]
The energies for the five steps of the reaction are

(1) \( 2 E_L = 2 (7.2) \text{ ev} \)

(2) \( \text{EA}_O \text{ (double)} = -5.12 \text{ ev} \)

(3) \( D^0 = 5.15 \text{ ev} \)

(4) \( -2 \text{EA}_O = -2 (1.46) \text{ ev} \)

(5) \( -2 E_L + 2 P^- = -2 (7.2 + 2.4) \text{ ev} \)

leading to the sum

\[ \text{EA}_O \text{ (double)} + D^0 = 2 \text{EA}_O + 2 P^- = 1.8 \text{ ev}. \]

Thus the energy of reaction (B) indicates that decomposition of the peroxide ion by dissociation into the singly charged oxide ions does not proceed to any significant extent. No polarization energy term is involved in step (1) of the reaction, since the crystal is polarized by unit charge both before and after removal of the peroxide ion from the crystal. However, the polarization energy is included in the energy for step (5), as the crystal is polarized before introduction of the singly charged oxide ions into the crystal but is not polarized following their incorporation.

The reaction (C) may be considered to be the sum of reaction (B) and the reaction

(\( D \) 2 \( O^- \) + 2 F centers → 2 \( O^{2-} \) + 2 negative ion vacancies.

The energy of reaction (D) is

\[ -2 (\text{EA}_O^- + 7.6) = 0.0 \text{ ev}; \]
therefore the energy of reaction (C) is the same as that of (B), or 1.8 ev.

Since peroxide ion does not decompose appreciably into any of the three ions $O^-$, $O^{2-}$ or $O_2^-$ under the conditions of additive coloration, it is the stable species of oxygen under these severe reducing conditions. The presence of a stoichiometric excess of negative ion vacancies is therefore assured. Under the severe oxidizing conditions attending growth of potassium chloride crystals in an oxygen atmosphere, however, oxygen is incorporated as the superoxide ion (66).

The Reduction Product of $\text{SO}_4^{2-}$ Involving the Sulfur Atom

As electron affinity data were not available for $\text{SO}_3^-$, $\text{SO}_2^-$ and $\text{SO}_3^-$, it was not possible to determine by thermodynamic argument the identity of the stable reduction product of sulfate ion which contains the sulfur atom. Sulfide ion in potassium chloride under the conditions of additive coloration is stable with respect to decomposition to $S^-$ ($\Delta E = 1.0$ ev), but the extent of reactions of the type

$$2\text{SO}^{2-} + 4F \text{ centers} \rightarrow 2\text{S}^{2-} + \text{O}_2^{2-} + 2\text{negative ion vacancies}$$

could not be determined. It seems reasonable to assume that the electron affinities of the singly charged species decrease in the order $\text{SO}_3^-$, $\text{SO}_2^-$, $\text{SO}^-$ and $S^-$, and, in view of the stability of the
sulfide ion, that the stable species will be a divalent anion.

The activity of the silver sulfide precipitated from a solution in which a colored crystal had been dissolved cannot be explained by the presence of sulfite ion, because of the solubility of silver sulfite. Further, the sulfite ion absorbs in the region 930-1000 cm\(^{-1}\), and the absence of such absorption in the infrared spectrum of the colored crystal is conclusive evidence of the absence of sulfite ion.

Sulfide ion cannot account for the absorption peak at 875 cm\(^{-1}\) in the infrared spectrum of the colored crystal so it is concluded that sulfate ion is reduced to thioperoxide ion, SO\(^{-}\), or to sulfoxylate ion, SO\(_2\)\(^{-}\). Either of these ions may reasonably account for the observed peak. The vibration frequency of \(^{35}\text{Cl}\,^{19}\text{F}\), which is isoelectronic with thioperoxide ion, is 793.2 cm\(^{-1}\) (32, p. 520).

Assuming no change in force constant from one ion to the other, \(^{32}\text{S}\,^{16}\text{O}^{-}\) should absorb at 850 cm\(^{-1}\). The antisymmetric stretch of \(^{35}\text{Cl}\,^{16}\text{O}_{2}^{-}\), isoelectronic with sulfoxylate ion, has a frequency of 844 cm\(^{-1}\) according to Duchesne and Brunelle (16). Again assuming no change in force constant, and neglecting coupling with other vibrational modes, one calculates the antisymmetric stretching frequency of \(^{32}\text{S}\,^{16}\text{O}_{2}^{-}\) to be 858 cm\(^{-1}\).

If sulfoxylate ion is the species present in colored KCl(K\(_2\)SO\(_4\)), the observed activity of the silver sulfide can be
explained by formation of thiosulfate ion from the sulfoxylate ion (67) and subsequent dismutation of thiosulfate ion into sulfide and sulfate ions by the silver ion (17). The chemistry of thioperoxide ion is unknown, but it seems reasonable that it would decompose in the presence of silver ion to give silver sulfide.

The reduction products of the sulfate ion greatly complicate the color center behavior of potassium chloride. Much further work will be necessary to elucidate this behavior. Discussion is limited to a few comments as to the probable nature of some of the absorbing centers.

\[ S_1 \text{ Center. The peak absorption energy of the } S_1 \text{ band is } 4.4 \text{ ev or approximately double that of the } F \text{ center, so the } S_1 \text{ band clearly cannot rise as a result of promotion of an electron localized in a vacancy aggregate. Neither is it attributed to the presence of } U \text{ centers through a hydride impurity in the potassium used for coloration; the absorption does not correspond to the } U \text{ or } U_2 \text{ band (13).} \]

As mentioned earlier, an absorption band called the alpha band appears in the tail of the fundamental absorption when a high concentration of free negative ion vacancies is present in an alkali
halide crystal. This band is attributed to the promotion of an electron to a vacancy from one of the 12 next-nearest neighbor chloride ions (3). In an analogous manner, it is suggested that the \( S_1 \) center consists of one of the divalent anions \( O_2^{2-} \), \( SO^{2-} \) or \( SO_2^{2-} \) and an associated negative ion vacancy, and that the \( S_1 \) band arises from promotion of an electron from the divalent anion to the vacancy.

The enhancement of the \( S_1 \) band resulting from heat treatment indicates an increase in the degree of association of negative ion vacancies and divalent anions. Quenching of the crystal to room temperature following coloration apparently leads to trapping of negative ion vacancies, forming centers with stability such that the crystal remains in a metastable state. Heat treatment then frees the negative ion vacancies and permits their association with the divalent anions, accompanied by enhancement of the \( S_1 \) band.

\( S_2 \) Center. Trapping of negative ion vacancies by \( F \) centers occurs during the course of \( M \)-center formation, and should occur in these crystals on quenching. If the resulting \( F^+ \) center has sufficiently low mobility, this center would be expected to be present in the crystals prior to \( F \)-light bleaching. The presence of the \( S_2 \) band in the spectrum prior to bleaching, and the thermal instability of the band, indicate that the band may arise from the \( F^+ \) center.
Other bands which appear in the spectrum on F-light bleaching may be due to higher analogs of the $F_2^+$ center, which are generally formulated as $F_n^+$.

**$S_3$ Center.** Since an $F_2^+$ center and a divalent anion will be attracted to each other electrostatically, they may associate to form a center of fairly high thermal stability. It is suggested that a center of this type may give rise to the $S_3$ band. The stability of the $S_3$ center exceeds that of the $M$ center, which is the most stable of the complex centers in pure potassium chloride.

**Summary**

Additive coloration of potassium chloride crystals doped with potassium sulfate leads to decomposition of the sulfate ion. Peroxide ion has been shown by thermodynamic argument to be one of the stable reduction products, and an infrared absorption peak appearing at 875 cm$^{-1}$ following coloration indicates that either thioperoxide ion, SO$_2^-$$^-$, or sulfoxylate ion, SO$_2$$^-$, is the reduction product involving sulfur.

Several new absorption bands were observed on F-light bleaching of the crystals. The $S_1$ band, located in the ultraviolet region at 284 m$\mu$, is felt to be an exciton band arising from association of one of the divalent anions and a negative ion vacancy. The $S_2$ band at 364 m$\mu$ may originate from the $F_2^+$ center.


