

Magnetism of KCl

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At room temperature KCl has a diamagnetic susceptibility of 1.04×10^{-6} cgs units per cm^3 . The value at liquid nitrogen temperatures is $\frac{1}{2}\%$ smaller. As the temperature is lowered further, a paramagnetic contribution inversely proportional to the temperature becomes apparent in additively or gamma-ray colored material. The magnitude of this paramagnetic contribution, which is proportional to the number of one-electron imperfection centers, is compared to the optical absorption of electron excess centers, to yield a value of 0.6 for the oscillator strength of the F band, and strong evidence that the M center is not paramagnetic. The results also indicate that the M center absorbs under the F band as well as in the M band.

I. INTRODUCTION

IN many materials it is possible, by measuring the magnetic susceptibility at low temperatures, to determine the concentration of magnetic centers to within a few percent. Such measurements therefore seem attractive for studying (paramagnetic) impurity and imperfection centers in solids. This is especially true when electron spin resonance techniques¹ are of limited usefulness. Electron excess color centers in alkali halides present just such a situation, since only a broad symmetric F center electron spin resonance absorption is observed.^{1,2}

Color centers have been studied for many years.³ The model of the F center, namely an electron trapped at a negative-ion vacancy, is firmly established. Moreover, a number of electron deficit (V -type) centers have been studied at low temperature by the spin resonance technique.⁴⁻⁷ As a result good models are available for these trapped hole centers and it is becoming apparent that there is not necessarily a one-to-one correspondence between obvious *major* optical absorption peaks and defect centers.⁸ In contrast to the hole (V -type) centers, there is still considerable disagreement about the configuration and modes of creation and destruction of electron-excess centers formed from F centers above room temperature. Long ago it was suggested³ that the M absorption band might be due to a cluster of an F center and neutral vacancy pair, while the R bands are due to paired F

centers. Recent experiments have yielded evidence^{9,10} that it is the M center that is composed of two F centers. As will be seen below, comparison of the magnetic susceptibility and optical absorption of KCl before and after bleaching of the F -absorption band yields further evidence for the " F_2 " or di- F center model of the M center.

The use of magnetic susceptibility measurements in the study of color centers is not new. Room temperature measurements¹¹ have been reported in connection with a study of colloid centers in KCl. Measurements at low temperature¹² have been used to determine the oscillator strengths of F centers in a number of alkali halides. The technique used in the present experiments is very similar to that used in the oscillator strength determinations; a result, obtained as a byproduct in the present work, is an additional value for the oscillator strength of the F band in KCl.

II. EXPERIMENT AND THEORY

A. Magnetic Susceptibility

When a solid is placed in a strong magnetic field gradient, there is a slight tendency for it to be either pulled into or expelled from the magnetic field. If we define the susceptibility k in terms of the magnetic moment M as follows,

$$k = M/H = -1/H[\partial(E/V)/\partial H], \quad (1)$$

where H is the magnetic field and E/V is the magnetic energy per unit volume of the sample, then it is seen easily that the force on the sample is given by

$$F = -\partial E/\partial x = -(\partial E/\partial H)(dH/dx) = kVHdH/dx. \quad (2)$$

In the Gouy and Faraday method of measuring the magnetic susceptibility, this force is measured with a sensitive balance.¹³ With the equipment used for the

* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

¹ A. F. Kip, C. K. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.* **91**, 1066 (1953).

² More detail can be obtained in some cases by the more difficult double resonance technique [G. Feher, *Phys. Rev.* **105**, 1122 (1957)].

³ See for instance review articles by F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954) and M. C. R. Symons and W. T. Doyle, *Quart. Revs. (London)* **14**, 62 (1960).

⁴ C. J. Delbecq, B. Smaller, and P. H. Yuster, *Phys. Rev.* **104**, 599 (1956).

⁵ T. G. Castner and W. Kanzig, *J. Phys. Chem. Solids* **3**, 178 (1957); T. O. Woodruff and W. Kanzig, *ibid.* **5**, 268 (1958).

⁶ W. Kanzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1959).

⁷ W. Kanzig and M. H. Cohen, *Phys. Rev. Letters* **3**, 509 (1959).

⁸ C. J. Delbecq, B. Smaller, and P. H. Yuster, *Phys. Rev.* **111**, 1235 (1958).

⁹ C. Z. VanDoorn, *Phys. Rev. Letters* **4**, 236 (1960); C. Z. VanDoorn and Y. Haven, *Ned. Tijdschr. Natuurk.* **26**, 216 (1960).

¹⁰ B. J. Faraday, H. Rabin, and W. D. Compton, *Phys. Rev. Letters* **7**, 57 (1961).

¹¹ A. B. Scott, H. J. Horostowski, and L. P. Bupp, *Phys. Rev.* **79**, 346 (1950).

¹² C. J. Rauch and C. V. Heer, *Phys. Rev.* **105**, 914 (1957).

¹³ See for instance, L. F. Bates, *Modern Magnetism* (University Press, Cambridge, 1948), p. 95 ff.

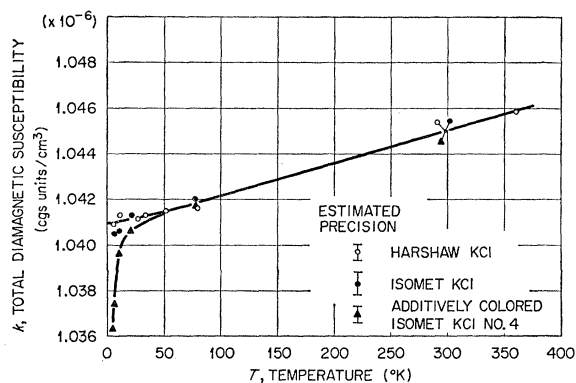


FIG. 1. The variation of the magnetic susceptibility with temperature of uncolored and additively colored potassium chloride.

present experiments,¹⁴⁻¹⁶ measurements are made between 2.5° and 300°K; changes of susceptibility with temperature are determined with a precision of 0.1%. The absolute value of k is obtained at room temperature by comparison with oxygen gas. Here errors of as much as 1% are possible.

In a system such as the alkali halides, where electrons are localized in filled shells at the various ions, only two contributions to the magnetic susceptibility have to be considered. One is the Langevin¹⁷ diamagnetism given by

$$k_d = -\frac{Ne^2}{6mc^2} \sum_i \langle r_i^2 \rangle_{av}, \quad (3)$$

where N is the number of atoms (ions) per unit volume, e and m are the electronic charge and mass, and $\langle r_i^2 \rangle_{av}$ is the mean square radius of the i th electron. The sum is over all the electrons of the atom or ion. The other contribution is the defect paramagnetism,¹⁸ given by

$$k_p = n\beta^2/kT, \quad (4)$$

where n is the number of paramagnetic centers and β is the Bohr magneton. It should be pointed out that assumptions of spin = $\frac{1}{2}$ and quenching of orbital moment of the unpaired electron at the defect are implicit in Eq. (4) as written.¹⁹ The lack of strong temperature dependence in the case of k_d and the inverse temperature dependence of k_p make it possible to separate the two contributions.

¹⁴ D. K. Stevens, J. W. Cleland, J. H. Crawford, Jr., and H. C. Schweinler, Phys. Rev. **100**, 1084 (1955).

¹⁵ D. K. Stevens, Oak Ridge National Laboratory Report, ORNL-1599 (unpublished).

¹⁶ E. Sonder and D. K. Stevens, Phys. Rev. **110**, 1027 (1958).

¹⁷ W. Pauli, Jr., Z. Physik **2**, 201 (1920).

¹⁸ See for instance J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

¹⁹ These are probably good assumptions when no transition metal elements are involved. ESR experiments have uniformly yielded $g \approx 2$ for centers in the alkali halides.

B. Optical Absorption

Most of the measurements were made at room temperature in a Cary model 14 spectrophotometer. A number of spectra were also run at liquid nitrogen temperatures in order to obtain better resolution of the M and R bands. In the determination of oscillator strengths, the Gaussian²⁰ form of the Smakula²¹ equation was used; i.e.,

$$nf = 7.2 \times 10^{15} \alpha \epsilon_{\frac{1}{2}}, \quad (5)$$

where α is the maximum absorption coefficient and $\epsilon_{\frac{1}{2}}$ is the half-width in ev.

C. Samples and Handling

Isomet and Harshaw crystals were used throughout this series of experiments. It should be pointed out that Harshaw KCl crystals contain an appreciable amount of water, which produces an absorption band at 2040 Å (see Fig. 4, curve c) and that in the Isomet crystals additive coloration produces a small absorption band near 2120 Å.²² There were also small absorptions observed near 2500 Å and 2900 Å in most of the additively colored crystals.

Additive coloration was achieved by heating the crystals together with potassium metal to temperatures in the neighborhood of 600–700°C in a copper bomb, one end of which (the end containing the K metal) could be held at a lower temperature. Coloring times of 1–2 weeks were used in most cases in the hope of obtaining uniform coloration. The samples were rapidly cooled by quenching the bomb in water. After coloration the samples were kept in the dark and handled under subdued red light.

Optical and susceptibility measurements were at first made on different samples, coming from adjacent

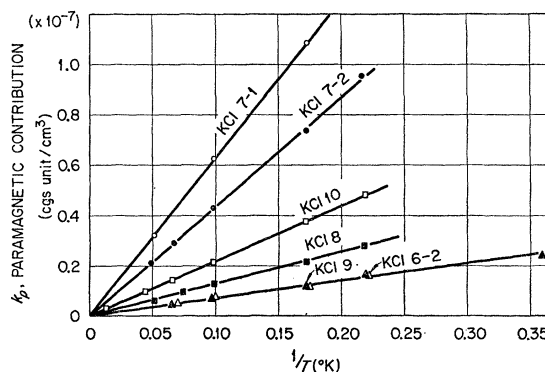


FIG. 2. Paramagnetic contribution to the susceptibility of a number of additively and gamma-ray colored specimens of potassium chloride.

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

²¹ A. Smakula, Z. Physik **59**, 603 (1930).

²² It is probable that this is the U band (KH^-) produced by dissociation of the OH^- during the coloration. [H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958)].

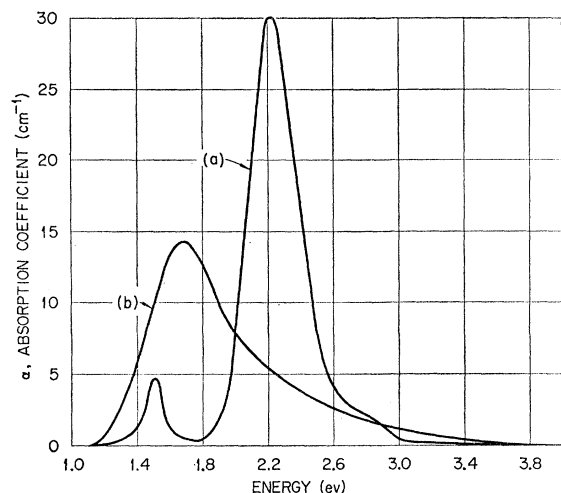


FIG. 3. Optical absorption of additively colored KCl. Curve (a) was obtained after coloration and rapid cooling. Curve (b) was obtained after the sample had been heated to 120°C.

portions of the colored ingots. However, in later experiments, especially those on gamma ray colored material, both types of measurements were made on the same samples.

III. RESULTS AND DISCUSSION

A. Uncolored KCl

Comparison of the magnetic susceptibility of KCl with that of oxygen gas¹⁴ (0.143×10^{-6} cm³ at 20°C)¹⁶ yields a value of $(1.04 \pm 0.01) \times 10^{-6}$ cgs units per cm³

for the diamagnetic susceptibility at room temperature. Slight additive coloration does not change this value. For comparison, the value quoted in the International Critical Tables is 1.024×10^{-6} and Heer and Rauch²³ report 0.97×10^{-6} .

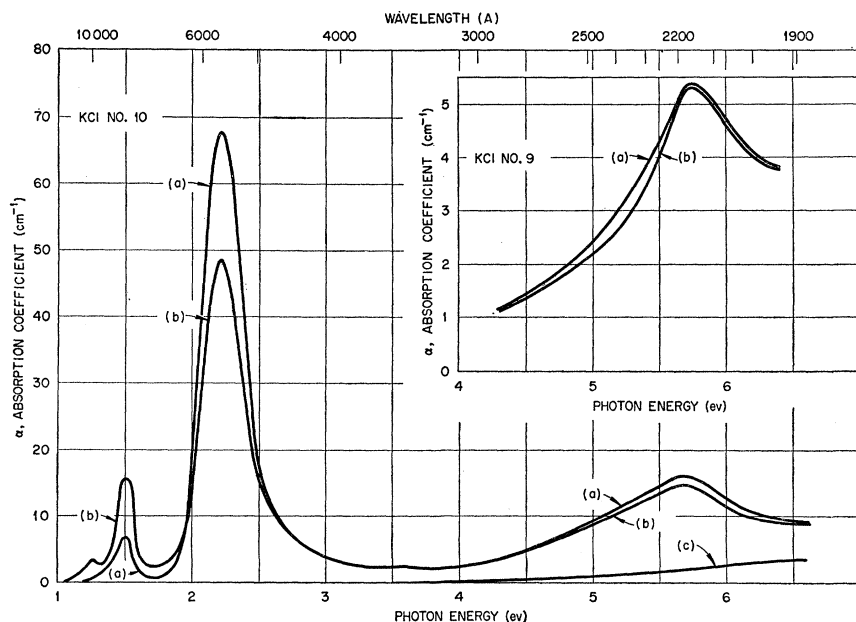
As shown in Fig. 1, the susceptibility decreases about $\frac{1}{2}\%$ when the temperature is lowered to liquid nitrogen or liquid helium temperatures. Such a decrease is not at all surprising in view of the fact that KCl becomes 2% more dense^{24,25} as the temperature is lowered. Thus, the linear dimensions of the crystal decrease by $\frac{2}{3}\%$. The decrease in the effective radii of the outer shell electrons, which are the most important contributors to the sum in Eq. (3) are of the same order of magnitude.

In Fig. 1, no paramagnetic $1/T$ contribution is discernible for the case of uncolored KCl. Comparison of the data with those of specimen 4b (also shown in the figure), containing 4×10^{16} magnetic centers per cm³, makes it evident that a few times 10^{15} magnetic centers can be detected. It is thus reasonable to assume that uncolored, commercial KCl contains less than $\sim 10^{15}$ paramagnetic impurities or imperfection centers per cm³.

B. F-Band Oscillator Strength

In Fig. 2 the paramagnetic contribution to the susceptibility of colored KCl at low temperature is plotted versus reciprocal temperature. According to Eq. (4), the slopes of the various curves give values for the density of magnetic centers. The curves labeled *a* in Figs. 3 and 4 show the optical absorption of

FIG. 4. Optical absorption of gamma-ray colored KCl. Curve (a) was obtained after coloration and before any light was permitted to fall upon the sample. Curve (b) was obtained after bleaching and annealing. Curve (c) shown for sample KCl-10 is included to indicate the magnitude of the OH⁻ absorption present in the uncolored material. The curves shown in the inset show the change in the shape of the absorption in the ultraviolet for sample KCl-9. See text for discussion.



²³ C. V. Heer and C. Rauch, Phys. Rev. **90**, 530 (1953).

²⁴ A. Henglein, Z. physik Chem. **115**, 91 (1925).

²⁵ R. Srinivasan, J. Indian Inst. Sci. **A37**, 232 (1955).

TABLE I. Oscillator strength results.

Ingot	Percent M centers ^a	Percent U and V centers ^b	No. optical plates measured	Range of nf^c (cm ⁻³)	n (from χ measurements) (cm ⁻³)	f^c
4			3	$(0.24-0.30) \times 10^{17}$	0.42×10^{17}	0.64
5			3	$(0.40-0.54) \times 10^{17}$	0.75×10^{17}	0.63
6-1	5		7	$(0.53-0.76) \times 10^{17}$	1.15×10^{17}	0.56
6-2 ^d	2		4	$(0.68-0.90) \times 10^{17}$	1.13×10^{17}	0.69
7-1			2	$(5.3-5.4) \times 10^{17}$	10.2×10^{17}	0.52
7-2 ^e	3		1	4.1×10^{17}	7.1×10^{17}	0.58
8	3		1	0.81×10^{17}	1.33×10^{17}	0.61
9	1	80	1	0.57×10^{17}	1.14×10^{17}	0.50
10	3	70	2	$(1.5-1.7) \times 10^{17}$	3.66×10^{17}	0.41

^a Ratio of band heights times 0.11 ev/0.35 ev.^b Ratio of band heights times 1.2 ev/0.35 ev.^c Assuming Gaussian line shape.^d After 5 months storage in dark.^e Stored 3 months and quenched.

additively colored and gamma-ray colored KCl, respectively. The main absorption in the visible region can be seen to be in the F band (2.2 ev), with a little (2-5%) absorption also taking place in the M band (1.5 ev). The uv absorption, which is not present in additively colored material, is probably a superposition of U and V bands. Under the assumption that the number of magnetic centers other than F centers is negligible, we have calculated F -band oscillator strengths from the optical absorption and magnetic susceptibility results. A Gaussian band shape and F bandwidth of 0.35 ev have been assumed. The results for all specimens are summarized in Table I. Ingots 4, 5, and 6 were additively colored Isomet crystals; 7, 8, 9, and 10 were Harshaw KCl, the first two additively colored, and the latter two gamma-ray colored.

A large variation in f is immediately apparent from the table. The variation would appear even more pronounced if each individual optical absorption measurement was used to calculate nf (and from that, f), rather than the average for a number of optical plates that had been cleaved from the susceptibility sample or from regions near it in the same ingot.

The extreme range of values of nf are indicated in the fifth column of Table I. The spread in oscillator strengths is about a factor of 5 larger than the expected errors in the measuring techniques. We have attempted to correlate the oscillator strengths with M -center density, total F -center concentration, and material source. However, no correlation was found. What was found was that in some otherwise uniformly colored ingots, some optical plates had appreciably different F bands as well as different ultraviolet absorptions. These variations also seemed to be random; thus, it seems that impurities and past history affect the coloring properties and oscillator strengths. Such effects would also explain the large differences reported for oscillator strength by different observers.²⁶⁻²⁹ Such values are listed in Table II. It is evident that the variation of reported values is of the same magnitude as the variations we have observed.

Comparison of oscillator strengths for the additively colored samples and gamma ray colored samples (shown below the line in Table I) would seem to indicate a somewhat smaller value for the irradiation colored samples. This difference, however, is smaller

TABLE II. Comparison with other investigators.

Date	Investigator	Method of ^a coloration	Technique ^b for determining number of centers	Range of F center concentration (cm ⁻³)	Average oscillator strength ^c
1936	Kleinschrod ^d	A	C	$4-10 \times 10^{17}$	0.55
1958	Doyle ^e	E	C	$1-11 \times 10^{17}$	0.62
1958	Scott and Hills ^f	A	C	$5-18 \times 10^{17}$	0.79
1956	Silsbee ^g	X	ESR	1×10^{17}	0.58
1957	Rauch and Heer ^h	A	χ	$5-9 \times 10^{17}$	0.45
1961	Present work	A γ	χ	$0.7-11 \times 10^{17}$	0.57

^a A=additive coloration by diffusion; E=additive coloration by electrolysis; X=x-ray irradiated; γ =Co⁶⁰ gamma-ray irradiated.^b C=chemical determination of excess metal; ESR=electron spin resonance absorption; χ =static magnetic susceptibility.^c Assuming Gaussian line shape, $f(\text{Gaussian})=0.679f(\text{Lorentzian})$.^d Reference 26.^e Reference 27.^f Reference 28.^g Reference 29.^h Reference 12.²⁶ F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).²⁷ W. T. Doyle, Phys. Rev. **111**, 1072 (1958).²⁸ A. B. Scott and M. E. Hill, J. Chem. Phys. **28**, 24 (1958).²⁹ R. H. Silsbee, Phys. Rev. **103**, 1675 (1956).

TABLE III. Change in F -band absorption and magnetism upon bleaching and annealing of KCl.

Sample 1	Treatment 2	$nf \times 10^{-17}$ 3	% M centers 4	% R and N centers 5	% colloid centers ^b 6	% F centers remaining after treatment 7	% F centers assuming ^c M absorption in F band 8	$n \times 10^{-17}$ 9	% magnetic centers remaining after treatment 10
6 ^a	Additive colored Bleached 6800 Å annealed 109°	14 days 32 hr; 1 hr	0.90 0.62	2 7½	1	4	69	1.13 0.61	53
7	Additive colored Bleached 3900 Å annealed 103°	14 days 13 hr; 1¼ hr	4.11 2.96	3 6	~½ 1	...	72	7.11 4.80	67
10	Gamma-ray colored Bleached 6900 Å annealed 111°	14½ hr 24 hr; 1 hr	1.70 1.22	3 7	72	3.60 2.30	63
9	Gamma-ray colored Bleached 6900 Å annealed 113°	1¾ hr 30 hr; 2 hr	0.57 0.28	1 2½	48	1.14 0.76	66

^a Ingot had been stored 5 months in dark after additive coloration.^b The colloid band is very broad and therefore difficult to resolve.^c See text for explanation.

than the random spread in values; it is not the order of a factor of 2, which would be expected if all the centers which absorb ultraviolet light in gamma-ray colored KCl were paramagnetic. At best, one of the minor contributors to the ultraviolet absorption (if, as is assumed, this absorption is due to more than one center) is paramagnetic. The major absorption center (probably the V_3) is probably nonmagnetic.³⁰ This would be consistent with the Cl_2^0 or (Cl_3^-) model³¹ of the V_3 center.

C. The Colloid Band

Curve b in Fig. 3 shows the broad band at 1.7 eV that is created upon annealing additively colored KCl in light at 120°C or slightly higher. Magnetic susceptibility measurements were performed before and after the anneal. From the slope of k_p vs $1/T$ plots (similar to Fig. 2), it was determined that for sample 6, the magnetic center concentration decreased from 1.1×10^{17} to less than 1×10^{16} as a result of creating the colloid band and destroying the F band. Evidently, centers absorbing in the colloid band are not paramagnetic.

D. Magnetic Changes during F - M Conversion

The results of optical and magnetic measurements before and after conversion of F centers to M centers are summarized in Table III. We shall discuss the three samples shown above the line first. Even though the bleach and anneal treatments³² were slightly varied,

³⁰ Comparable oscillator strengths in additively and irradiation colored KCl have also been reported by F. J. Reid, R. T. Bate, and C. V. Heer, *Bull. Am. Phys. Soc.* **2**, 154 (1957).

³¹ J. H. Crawford, Jr., and C. M. Nelson, *Phys. Rev. Letters* **5**, 314 (1960).

³² The bleach and anneal treatments differ slightly for the various samples. An attempt was made, using practice samples

the results are qualitatively similar for the two additively colored and one of the gamma ray colored samples. Columns 4-7 give the density of the various centers in the samples after the stated treatments, as deduced from the optical absorption. The densities are written as percent of the *original* F -center concentration in the sample, shown by the *upper* of the pair of numbers for each sample in column 3. Columns 9 and 10 give the density of magnetic centers, as obtained from susceptibility measurements, the percentage in this case being of the number of *magnetic* centers in the originally colored specimen.

Comparison of columns 7 and 10 immediately shows that the decrease in magnetic centers is appreciably greater than the decrease of the F -band absorption.^{33,33a} If the F -center electrons were forming even in part paramagnetic cluster centers (as for instance M centers of the type suggested by Seitz³), the opposite would happen and the density of paramagnetic centers would decrease more slowly than the F -band absorption. Even if no new paramagnetic centers were created upon destruction of F centers, the percent change in columns 7 and 10 would be the same.

Recently a nonmagnetic model has been proposed^{34,35}

from the same ingots to determine conditions that would for each specimen create *uniformly throughout the volume* the maximum M -center concentration, consistent with reasonably small amounts of colloid and R centers.

³³ Comparison between changes in spin resonance and optical absorption, resulting from bleaching KCl, was made a few years ago. Results qualitatively similar to the present ones were reported. [J. Lambe and J. A. Baker, *Bull. Am. Phys. Soc.* **3**, 136 (1958)].

^{33a} Note added in proof. Also see more recent results of H. Cross, *Z. Physik* **164**, 341 (1961).

³⁴ C. Z. VanDoorn and Y. Haven, *Philips Research Repts.* **11**, 479 (1956).

³⁵ H. Pick, *Z. Physik* **159**, 69 (1960).

for the M center. This M center would absorb both in its own (M) absorption band and under the F band. It is composed simply of a pair of adjacent F centers. Light with a wavelength corresponding to the M band would be absorbed only when its polarization is parallel to the M -center axis. Light polarized in one of the two perpendicular directions would see an F -center-like charge distribution, causing those photons with energies corresponding to those within the F band to be absorbed. Qualitatively, according to this model the *true* F center absorption of our specimens after the bleach and anneal treatments should be the measured absorption *minus* twice the absorption in the M band.^{36,36a} Column 8 lists these values, again in percentages of the original F -center density. The agreement between column 8 and 10 is surprisingly good.³⁷

Below the line in Table III are shown results of measurements on a gamma-ray colored sample (KCl-9) which contained only 1×10^{17} F centers per cm^3 . This concentration is probably not much greater than the density of impurity ions.³⁸ Thus, the fact that in this case the F -band absorption decreased more than the susceptibility is not too surprising.³⁹ In all the samples, an appreciable number of F centers (and corresponding magnetic centers) disappeared without forming M centers. Evidence of (nonmagnetic) colloid band formation was found, especially in the case of the additively colored crystals; in the gamma-ray colored

specimen (KCl-10), there was a significant decrease of the uv absorption during the bleaching treatment. In the case of the anomalous specimen (KCl-9), however, even though the F band decreased much more than in any other sample, there was little decrease in the *peak* of the uv absorption. However, the *form* of the absorption band in the ultraviolet changed appreciably, as shown in the inset in Fig. 3. It seems reasonable, therefore, to propose that the bleach and anneal in the case of sample KCl-9 created in part magnetic impurity centers and an absorption in the same wavelength range as the U and V absorption bands.⁴⁰

IV. CONCLUSIONS

A. The room temperature susceptibility of KCl is -1.04×10^{16} cgs units/ cm^3 . A half-percent decrease in the susceptibility between room and liquid nitrogen temperatures is of the magnitude one would expect due to the increase in density of the material.

B. Commercial (Isomet or Harshaw) KCl contains less than $\sim 10^{15}$ magnetic centers per cm^3 before coloration. However, variations in coloration and bleaching properties suggest that nonmagnetic impurities or imperfections, which might influence this behavior, are present in concentrations exceeding $10^{16}/\text{cm}^3$.

C. The oscillator strength of the F band was found to be 0.57 ± 0.08 .

D. The center responsible for the main part of the uv absorption (probably V_3) in KCl colored with gamma rays at room temperature is not paramagnetic. However, the data indicate that a subsidiary hole center may be paramagnetic.

E. The colloid center in KCl is not paramagnetic.

F. The M center is not paramagnetic; it most probably has an absorption band under the F band as well as in the M band. The di- F center model is in agreement with the experimental results.

ACKNOWLEDGMENTS

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³⁶ This is a purely qualitative argument, in which oscillator strengths of 1 and $\frac{1}{2}$ are assumed, respectively, for the F and each of the three M absorption bands. The ratio of M -center absorption in the M band to that under the F band is discussed by Pick (reference 35) and also by T. Tomiki, J. Phys. Soc. Japan **15**, 495 (1960).

^{36a} Note added in proof. Recent measurements of anisotropy in the F and M band absorption of KCl made at liquid N_2 temperatures [F. Okamoto, Phys. Rev. **124**, 1090 (1961)] indicate that the absorption at the F -band maximum due to the M center may be somewhat less than the M -band absorption, rather than twice the latter, as is assumed here. If this is true at room temperature as well, then the numbers in column 8 of Table III would be higher. The conclusions quoted herein, however, are not changed.

³⁷ It might be argued that for the case of the gamma-ray-colored sample KCl 10, the F -center oscillator strength results hint at the possibility that one of the V bands might be paramagnetic and that a loss of such paramagnetism as a result of bleaching and annealing should be taken into consideration. Figure 4 shows that the V absorption did not change shape and decreased about 7%. If even as many as half the bleached V centers had been magnetic this would still only make a difference of 3-4%, raising the number of magnetic F centers remaining (column 10 of Table III) from 63 to 67%. This is still less than the remaining F -band absorption.

³⁸ The total irradiation flux used was 3×10^6 r, which was not enough to carry the sample very far into the second stage of coloration. Since first stage coloration has been attributed to impurity contributed vacancies [see for instance, W. E. Bron, Phys. Rev. **119**, 1853 (1960) and references given therein], the concentration of F centers and impurity ions should be comparable.

³⁹ It might also be noted that in this particular sample, due to a longer annealing time, only a $1\frac{1}{2}\%$ increase of M centers was produced, thus making it more easy for impurity effects to swamp the changes created by the M -center production.

⁴⁰ The U center is not paramagnetic (reference 4). However, the oxygen atoms from the original OH^- are likely candidates for forming magnetic centers.