the mobility of the negative vacancies (as members of pairs) the overlapping of absorption bands would lead to a broad band exhibiting the behavior of the R'-band. Among the R'-centers, particularly during early stages, will undoubtedly be found the R- and M-centers. There is no certainty that the R'-centers formed thermally are precisely the same as those formed by heating combined with irradiation; indeed Fig. 5 shows considerable difference in the R'-band formed thermally and that formed by irradiation of samples of the same colored crystal. The size of the R'-centers is probably not great, certainly not of colloidal size, and at temperatures above 300°C noticeable dissociation into F-centers and vacancies becomes apparent. At 510°, dissociation into F- and M-centers is virtually complete.

(c) The shift of maximum in the R'-band with variation in equilibrium temperature is undoubtedly related to the increasing mobility of negative-ion vacancies with temperature which should lead to the rapid formation of aggregates containing several F-centers by direct diffusion and combination.

Further experiments are being undertaken in this laboratory to establish more fully the structure and physical properties of the R-, M- and R'-centers.

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The Paramagnetism of Color Centers in KCl*

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Two methods for studying susceptibility changes occurring during thermal and optical alterations in color centers in KCl are described. The magnetic changes accompanying formation of R'-centers from F-centers, and upon completely destroying both F- and R'-centers, indicate that the moment of a F-center is that calculated for an s-electron, that R'-centers have a variable moment depending on the distribution of centers, but generally very nearly that of F-centers, and that irradiation during R'-center formation results in a destruction of paramagnetism.

I. INTRODUCTION

THE theory of color centers in alkali halides has been reviewed by Mott and Gurney[1] and by Seitz.[2] The interpretation of a variety of experiments on the optical and electrical properties of crystals colored both by radiation and by the addition of a stoichiometric excess of alkali metal has led to some quite definite ideas regarding the nature of the absorbing centers. A F-center is considered to consist of an electron trapped in a halide ion vacancy. Such trapped electrons behave optically very much as s-electrons, and since they are unpaired, the presence of F-centers should impart a small paramagnetic susceptibility to the over-all diamagnetism of the salt, given by

$$\kappa = n\beta^2/kT,$$

where n is the concentration of F-centers/cc, β is the Bohr magneton, and k is Boltzmann's constant. Jensen[3] succeeded in measuring the decrease in diamagnetism of a KBr crystal containing a small amount of KH when F-centers were produced by ultraviolet illumination; the agreement with the decrease calculated from this equation, was very good in view of the experimental difficulties involved. His experimental moment for a F-center was about 10 percent below that for an unpaired s-electron in a free atom but it is doubtful whether the difference is significant.

In order to provide further confirmation of the theory of F-centers and to permit a study of the magnetic changes accompanying the formation and destruction of other color centers in alkali halides,[4] methods have been developed for the measurement of the small susceptibility changes occurring in additively colored crystals when subjected to thermal and optical treatments.

The expected change in volume susceptibility as a densely colored alkali halide, containing for example 10^{19} F-centers/cc, is de-colorized completely by prolonged heating in vacuum is about 2×10^{-8} c.g.s. unit; in the case of KCl this represents a 2 percent increase in diamagnetism. Although this change can be conveniently detected for samples which may remain in place during a magnetic transformation, for samples requiring removal from the magnetic balance for extended thermal treatment and later replacement upon the balance, the errors due to positioning in the field

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[1] Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940).

[2] F. Seitz, Rev. Mod. Phys. 18, 384 (1946).

[3] P. Jensen, Ann. d. Physik 34, 161 (1939).

[4] Such as R-, M-, and R'-centers, discussed by Scott and Bupp, Phys. Rev. 79, 341 (1950), preceding paper.

are sufficient to mask a 2 percent change occurring during the treatment. To overcome positional errors, a differential magnetic balance has been designed which detects the change, due to susceptibility changes, in the equilibrium position of a sample in the field of a small magnet. A second magnetic balance utilizing a strongly non-homogeneous field, and referred to hereafter as the Faraday balance, was designed to observe magnetic changes in colored crystals upon arc-light illumination of the crystal *in situ*.

A group of experiments on the susceptibility changes accompanying the complete destruction of F- and R'-centers in KCl, and the thermal conversion of F- to R'-centers was carried out by means of the differential balance; changes accompanying the conversion of F- to R'-centers by arc light irradiation were studied by means of the Faraday balance. KCl colored with excess K was used in all cases for the reasons given in reference 4.

II. EXPERIMENTAL

(A) Differential Magnetic Balance

Figure 1A illustrates schematically the principle of the differential balance. The balance beam of fine glass tubing was suspended by a 10μ quartz fiber from an adjustable brass mounting. At one end of the beam, between the poles of an Alnico permanent magnet, was rigidly suspended a V-shaped glass trough in which was cemented a plain KCl crystal (D) of length 2.7 cm and cross section about 0.13 cm^2. The sample under investigation (C), of about the same dimensions, was laid in the trough and butted up against D. In this way its position in the carrier could be reproduced, upon removing and replacing, with accuracy. Beneath the glass trough was suspended a 4-mm o.d. glass tube filled with a mixture of MgO and $NiCO_3$, in such proportions that the entire assembly, including the two crystals, was very slightly paramagnetic. The adjustment of this proportion and the cross section of the crystals was done by trial-and-error until the assembly came to rest with the inner end of D at about the center of the homogeneous portion of the field. The restoring force for small displacements from the equilibrium position depended on the field-strength gradients at the outer ends of the crystals, trough and tube, on variations of cross section and susceptibility and corresponding field-strength gradients along the axis of the assembly, and on the torsional constant of the quartz fiber. This force could be made as small as desired by reduction in the proportion of $NiCO_3$ in the mixture. The rotational period of the balance at optimum sensitivity was about 20 seconds.

Variations in equilibrium position were followed by scale readings in the micrometer eyepiece of the traveling microscope M. The force necessary to give a particular displacement was obtained from the current through the solenoid S, which acted upon a tube of $NiCO_3$ of known susceptibility. For these experiments the sensitivity was about 7×10^{-5} dyne/μ. The change in volume susceptibility of C during a thermal treatment was related to the change in equilibrium position of the assembly before and after by the equation

$$\Delta\kappa=2dS/[A(H_1^2-H_2^2)],$$

where d is the displacement of equilibrium position in μ, S is the sensitivity in dynes/μ, A is the cross-sectional area of C, H_1 is the field at the inner end, and H_2 at the outer end of C.

The entire balance was mounted upon a heavy marble slab resting on rubber cushions, and was surrounded by a draft-proof case and a second larger curtained enclosure to reduce thermal variations. The crystal carrier was illuminated through a double glass window by fluorescent light.

Magnetic field determinations were in all cases made by means of a small flip-coil and ballistic galvanometer which were calibrated in the field of a large electromagnet which had been accurately measured by means of its force on a $NiCl_2$ solution of known susceptibility.[5] The susceptibility of the $NiCO_3$ tube (in the solenoid) was measured in terms of κA for the tube plus contents at field strengths of 4650 and 1740 oersteds, as a test for ferromagnetic impurities. Values at the two field strengths agreed within the small experimental error and justified the extrapolation to the much smaller field in the solenoid. The field of the permanent magnet of the balance was measured before and after the data were obtained, and as the strength varied only 0.2 percent during a period of three months, the final value, 4560 oersteds, was used for H_1. The value of H_2 was 1310 oersteds. The current through the solenoid, of

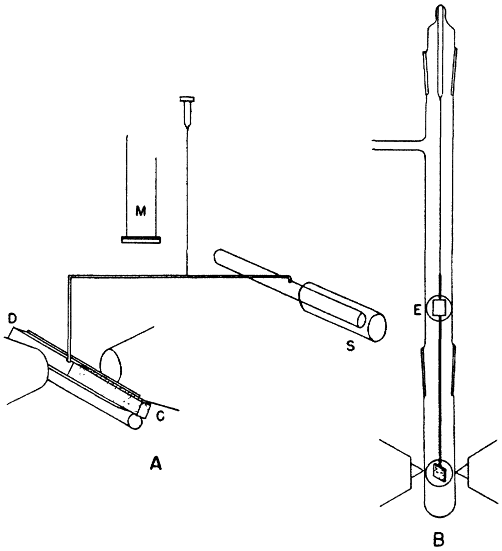

FIG. 1. A. Differential magnetic balance. B. Faraday magnetic balance.

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[5] P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1943), pp. 26, 46.

109.2 turns/cm, was measured by a calibrated ammeter. Errors in electrical and magnetic field measurements were in general negligible as compared with analytical errors and errors in measuring balance displacements.

Susceptibility changes were determined by observing the average rest position of the outer end of sample crystal as it was repeatedly removed and replaced in the carrier trough and the average rest position after it was subjected to a particular thermal treatment. The purpose of obtaining average values based on removing and replacing the crystal was to reduce the observational error due to variation in the position of the crystal in the trough as it was removed from and replaced on the balance. Actually it was found that there was a slow periodic drift of rest position, and to avoid error from this source the position of the sample crystal was measured in terms of a reference crystal of the same dimensions which was placed on the balance alternately with the sample. The average positional difference between sample and reference before treatment was subtracted from the average difference after treatment to obtain the displacement corresponding to the magnetic change produced. Sufficiently many observations were made, usually about 16 before and 16 after treatment, to reduce the probable observational error of the displacement to 6μ or less. The relative observational error, in the case of a volume susceptibility change of 2×10^{-8} c.g.s. unit in a crystal of cross section 0.13 cm^2, was 1.5 percent. The current through the solenoid required to give an equal displacement in the opposite direction was then measured by repeated observations with the current on and off.

The change in atomic susceptibility of the stoichiometrically excess K occurring during a particular treatment can be computed directly from the solenoid current by the equation

$$\Delta\chi_M=\left[\frac{\kappa_1 A_1(0.4\pi N_S)^2 l_1 N}{l_2(H_1{}^2-H_2{}^2)}\right]\frac{I^2}{An},$$

where $\kappa_1 A_1$ is the product of volume susceptibility and cross-sectional area of the $NiCO_3$ and tube, N_S is the number of turns/cm for the solenoid, l_1 and l_2 are the distances from the $NiCO_3$ tube and the crystal carrier to the quartz fiber suspension (11.9 and 17.4 cm respectively), N is Avogadro's number, I is the solenoid current, and A is the cross-sectional area and n the concentration of excess K, in atoms/cc, of the sample crystal.

The Faraday balance, Fig. 1B, served to measure susceptibility changes occurring when crystals containing color centers are irradiated by the arc light. The sample crystal, about $10\times5\times2$ mm, mounted on a 0.1-mm glass rod by means of a glass spring clip, was suspended by a 5μ-quartz fiber approximately 50 cm long. The crystal could be rotated by a vacuum-tight torsion head, and its position followed by means of the mirror *E*, together with a lamp and scale. The field of an Alnico permanent magnet was rendered strongly non-homogeneous by two cone-shaped pole tips and the position of the magnet and torsion head so adjusted that the long axis of the crystal lay quite nearly along the axis of the poles. This was found to be the position of maximum sensitivity.

TABLE I. Change in molar susceptibility of color centers in KCl during certain processes.

		Differential balance		
$n\times10^{-19}$	A(cm^2)	I(amp)	Process	$\Delta\chi_M\times10^3$
0.66	0.130	0.67	F, $R'\rightarrow$decol.	1.2
1.1	0.127	1.06	F, $R'\rightarrow$decol.	1.8
1.1	0.135	0.78	F, $R'\rightarrow$decol.	0.96
		Average	F, $R'\rightarrow$decol.	1.3±0.3
1.7	0.130	0.00	F, $R'\rightarrow R'$	0.00
1.3	0.130	0.48	F, $R'\rightarrow R'$	0.32
1.1	0.135	0.63	F, $R'\rightarrow R'$	0.62
		Average	F, $R'\rightarrow R'$	(0.3)
1.7	0.130	0.56	$R'\rightarrow$decol.	0.33
1.3	0.126	0.84	$R'\rightarrow$decol.	1.0
		Average	$R'\rightarrow$decol.	(0.7)
		Faraday balance		
$n\times10^{-19}$	P_{air}(mm)	$\kappa\times10^8$	Process	$\Delta\chi_M\times10^3$
1.1	630	2.4	F, $R'\rightarrow R'$	1.3
1.3	570	2.2	F, $R'\rightarrow R'$	1.0
1.3	750	2.9	F, $R'\rightarrow R'$	1.3
		Average	F, $R'\rightarrow R'$	1.2±0.2

The apparatus was calibrated by evacuating and observing the change of position of the crystal at several pressures as air was readmitted. From the known volume susceptibility of air the lamp-and-scale reading was then known as a function of the change in volume susceptibility of the sample. The calibration was repeated using oxygen and CO_2 to establish that there was no rotational effect associated with the buoyancy exerted by the gases; the rotation per cm oxygen was about five times that of air and for CO_2 was about 10 percent of that of air and in the opposite direction, which is to be expected from the relative susceptibilities. The air calibration was repeated for each sample studied, as it was strongly dependent upon crystal size and position in the field.

Susceptibility changes were measured by determining the rest position of the sample colored crystal, the apparatus being evacuated, and again after about 15 minutes of strong illumination, through a quartz window, with an arc lamp. The change in molar susceptibility for the color centers was computed from the relation

$$\Delta\chi_M=(PN\kappa_a)/760,$$

where P is the pressure of air in mm giving an equivalent positional change and κ_a is the volume susceptibility of air at 760 mm and 20°C (assumed to be 2.90×10^{-8} c.g.s. unit).

The thermal changes occurring in the apparatus during illumination caused a large temporary positional change, but when a sample of pure KCl was used for repeated measurements, it was found to return to its initial position after the treatment, with a probable error of 1.6 cm, measured on the scale. Since the magnetic displacements were between 6 and 13 cm, this represents an observational error of from 12 to 25 percent.

The preparation of colored crystals, analytical methods, and thermal and optical processes of altering color centers have been discussed in reference 4. All concentrations were determined by the *p*H-change method.

III. RESULTS

The changes in susceptibility during the following processes were measured by means of the differential balance.

(a) Crystals containing a high concentration of *F*- and *R'*-centers were heated at 300° for 15 minutes to convert all, or nearly all, centers to *R'*-centers. Absorption curves for densely colored crystals before and after this treatment were all similar to curves 1 and 2, Fig. 5, of reference 4. This process is referred to as $F, R' \rightarrow R'$.

(b) Crystals containing a high concentration of *F*- and *R'*-centers were heated in vacuum at 500–600°C until they appeared to be colorless. Absorption measurements after the process showed no absorption in the visible region, but considerable in the near ultraviolet which was probably due to a residue of K_2O in the lattice. This process is referred to as $F, R' \rightarrow$decol.

(c) Crystals treated as in (a) were decolorized as in (b). This process is referred to as $R' \rightarrow$decol.

The change in molar susceptibility, calculated on the basis of the excess K as determined from *p*H measurements, for these processes is tabulated in Table I.

It will be noted that the average decrease in molar susceptibility as a crystal containing a mixture of *F*- and *R'*-centers is completely decolorized is $(1.3\pm0.3)\times10^{-3}$ c.g.s unit. The estimate of error is based on the observed deviations and the estimated analytical error. The theoretical molar susceptibility for free atoms having one *s*-electron each is 1.28×10^{-3} unit at 25°C. The decrease in susceptibility as *F*-centers are converted to *R'*-centers thermally was non-reproducible but was small, on the average; similarly, the decolorization of crystals containing only *R'*-centers gave a non-reproducible susceptibility change, on the average less than that expected for the same amount of K in the form of free atoms.

These data may be interpreted, in view of the suggestions made in reference 4, in the following way: since *R'*-centers are a variety of small aggregates containing one or more *F*-centers and lattice-vacancies, a considerable paramagnetism should arise from centers having an odd number of electrons, such as the F_2^+-center or the combination of an *F*-center and a pair of vacancies. Centers containing 3*F*-centers would contribute one-third of the paramagnetism of an equal number of *F*-centers, and so on. Thus we expect that as the concentration and temperature at which the *R'*-centers are established varies there would be a range of paramagnetism due to the variation in distribution of the types of *R'*-centers; it would approach the paramagnetism of *F*-centers under condition favoring the formation of aggregates containing only one *F*-center. This conclusion is borne out by the variations in $\Delta\chi_M$ for different crystals undergoing heat treatment to form *R'*-centers or decolorization of crystals containing *R'*-centers. It is evident that, on the average, *R'*-centers have a paramagnetism not much less than *F*-centers.

The value of $\Delta\chi_M$ accompanying irradiation of color centers by arc-light, as measured upon the Faraday balance, is also given in Table I. The estimated error was obtained as above. It is surprising to note that during arc-light irradiation a decrease in paramagnetism very nearly equal to that produced by complete decolorizing is observed.

Comparison of curve 3 with curve 2, Fig. 5, of reference 4, indicates that *R'*-centers produced by irradiation do not absorb exactly as do *R'*-centers produced thermally, at least in densely colored crystals. It is likely that during excitation most or all of the centers will be ionized and that electrons may move through the conduction levels from trap to trap until a very stable set of centers is produced. Centers having an even number of electrons in the form of pairs would be a probable result, and the paramagnetism of the original *F*- and *R'*-centers would be destroyed. Additional experiments to show whether there are any other observable differences between *R'*-centers produced thermally and those produced by a combination of illumination and heating would be very desirable.

It must be emphasized that the foregoing results cannot be interpreted in a precise way, particularly due to lack of information on the concentration of *R'*-centers as such. It is significant, however, that the magnetic data is in general consistent with the suggestions made in reference 4 in regard to the structure of *R'*-centers. It may also be concluded that the moment of the *F*-centers is adequately predicted by theory, if allowance be made for the paramagnetism of the accompanying *R'*-centers.