

$$\sigma_x = \frac{\sigma}{1+i\omega\tau} \left[\frac{3\pi}{4a} \coth(\pi\gamma) - \frac{3}{a^2} + \frac{3\pi}{4a^3} \coth(\pi\gamma)(1+\frac{3}{4}\gamma^{-2}) + \dots \right]. \quad (36)$$

As this expression differs from the expansion of σ_{zz} only in the third term, the surface impedance $Z_x=Z_z$, in the approximation considered in this note.

The power absorbed by the metal turns out to have a series of maxima and minima of the same nature as that predicted in Sec. I. As $Z_x=Z_z$, we have shown

that the position and intensity of the peaks and the width of the resonant lines are identical in both longitudinal and transverse cyclotron resonance, provided that the metal under investigation is in the extreme anomalous skin effect region.

ACKNOWLEDGMENTS

The author wishes to thank Dr. V. Heine for suggesting this problem and Dr. P. W. Anderson, Professor C. Kittel, and Dr. B. Rosenblum for useful discussions. This work was done during the tenure of the Whiting Fellowship in Physics at the University of California, Berkeley.

Some Low-Temperature Properties of the *R*, *M*, and *N* Centers in KCl and NaCl

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(Received August 13, 1958)

Temporary changes in the absorption spectrum of a colored NaCl crystal can be produced at 77 and 4°K by irradiating the crystal with a strong auxiliary light. The changes in the absorption spectrum indicate that the *R*, *M*, and *N* centers are not randomly distributed but are located near each other. It is concluded that previous arguments based upon less complete observations are not valid and that one cannot decide from this type of experiment whether the *R*₁ and *R*₂ bands arise from transitions in two distinct centers or from two transitions in the same center. Measurements of the degree of polarization of the emission excited with *R*₁- or *R*₂-band light indicate that the concentration of other centers probably affects this number. It is concluded that this measurement may not determine the symmetry of these centers. Measurements of the temperature dependence of the half-widths of the absorption and emission bands of the *M* center indicates that the optical transition is primarily influenced by local interactions of the center with neighboring ions and not by interactions with the long-range phonons of the lattice.

INTRODUCTION

TWO prominent optical absorption bands lie between the *F* and *M* bands in the alkali halides. These have been called the *R* bands and the centers giving rise to these absorptions are called *R*₁ and *R*₂. The most usual treatments for the production of these bands consist of optically bleaching the *F* band in additively colored crystals or of extensively irradiating the crystals with ionizing radiation. Both operations are done at room temperature.

Although the mechanism of production of these centers is not well established it has been suggested that these centers result from the coagulation of *F* centers. A consideration of the kinetics of the coagulation led Seitz to suggest that the *R*₁ center consists of an electron trapped at a pair of negative-ion vacancies and the *R*₂ center consists of two electrons trapped at a pair of negative-ion vacancies.¹

The observation that the ratio of the peak heights of the *R*₁ and *R*₂ bands is nearly constant for a large variation in the concentration of the centers led

Herman, Wallis, and Wallis to suggest that both absorption bands arise from transitions in the same center.² They suggested that the center consists of two electrons trapped at a pair of negative-ion vacancies. The *R*₂ band results from the electronic transition from the ground state to the first excited state while the *R*₁ band results from the electronic transition from the ground state to the second excited state. These authors found reasonable agreement between the energies of the peak absorption of these bands and the transition energies calculated on the basis of their model.

Lambe and Compton have argued that both absorption bands cannot arise from transitions in the same center.³ This was based upon the observation that irradiation at 77°K with an auxiliary *R*₁-band light bleached the *R*₁ band but did not affect the *R*₂ band. When the auxiliary *R*₁-band light was removed, the absorption in the *R*₁ band returned to its original value. It was argued that both bands should be bleached by the auxiliary *R*₁ light if the same center is responsible for both bands.

² Herman, Wallis, and Wallis, *Phys. Rev.* **103**, 87 (1956).

³ J. Lambe and W. D. Compton, *Phys. Rev.* **106**, 684 (1957).

¹ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

Studies of the degree of polarization of the *R*-center emission at 77°K have led to different conclusions concerning the symmetry of these centers. Lambe and Compton³ concluded that both *R* centers have $\langle 110 \rangle$ symmetry while van Doorn⁴ concluded that both centers have $\langle 111 \rangle$ symmetry. In neither case is the polarization as great as would be expected from a simple dipole aligned along the above directions.

The results of a more extensive study of the temporary bleaching effect and the degree of polarization of the luminescence will be described in this paper. The arguments concerning the models of the *R* centers will be examined in terms of these new data. In addition some preliminary results on the nature of the interaction of the *M* center with the lattice will be given.

RESULTS

Temporary Bleaching

The experimental arrangement used to study the temporary bleaching effect was similar to that used before and is shown in Fig. 1.³ The crystal was contained

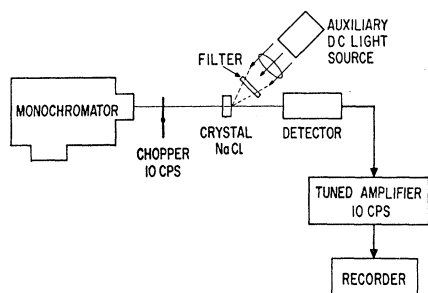


FIG. 1. Block diagram of the equipment used to study the temporary bleaching effect.

in a previously described helium Dewar that had been modified by the addition of a quartz window placed at right angles to the direction of light transmission.⁵ The sample was cooled by conduction to temperatures near 77 or 4°K. Although the exact temperature was uncertain, the sensitivity of this measurement was greater than that of the previous work since the sample was not immersed in the bubbling liquid nitrogen.³ The dc auxiliary light consisted of a 300-watt tungsten lamp and appropriate filters so that various wavelength regions could be used.

The data of Figs. 2 and 3 were taken as follows. The transmission of the sample at a given wavelength was measured. The auxiliary dc light was turned on and the change Δ in the transmission was noted. The auxiliary light was then removed and the transmission was noted to return to its original value. This procedure was repeated for wavelengths between 3300 and 12 000 Å for each wavelength setting of the auxiliary light. A

⁴ C. Z. van Doorn, Philips Research Repts. 12, 309 (1957).

⁵ G. A. Russell and C. C. Klick, Phys. Rev. 101, 1473 (1956).

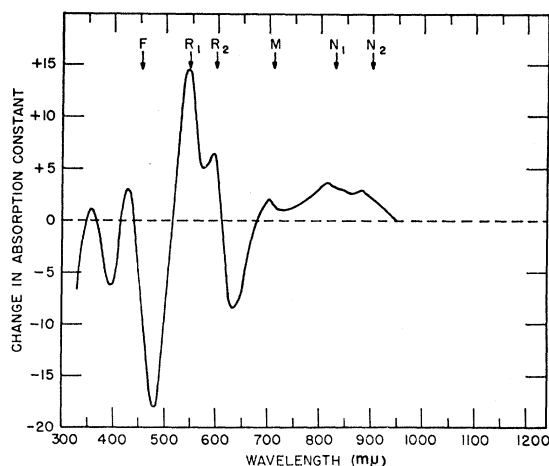


FIG. 2. Temporary change in absorption in NaCl at 77°K produced by irradiation with R_1 -band light. A positive change in absorption coefficient corresponds to a bleaching of the number of absorbing centers. The location of the peak of the absorption bands are indicated by the arrows.

positive Δ results when the absorption decreases and a negative Δ when the absorption increases.

If I is the intensity of the transmitted light with the auxiliary light off and $I \pm \Delta$ the intensity of the transmitted light with the auxiliary light on, then the change in the absorption constant is proportional to $\pm \Delta/I$ for small Δ . The light signal was adjusted so that I was constant for all readings. Thus, in a given sample, Δ is proportional to the change in the absorption constant or to the fractional change in the number of centers absorbing at a given wavelength.

Figure 2 shows the results at 77°K for auxiliary

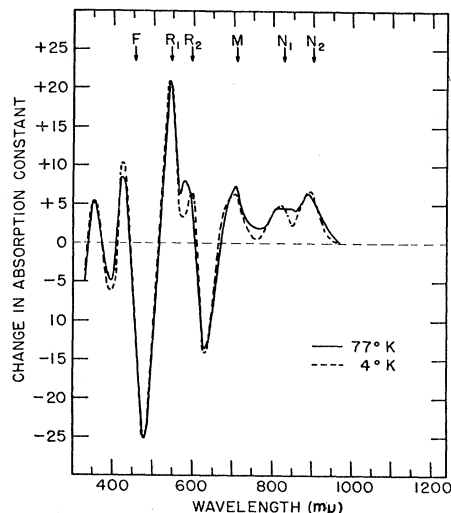


FIG. 3. Temporary change in absorption in NaCl produced by irradiation with N_2 -band light. Crystal temperature — 77°K, - - - near 4°K. A positive change in absorption coefficient corresponds to a bleaching of the number of absorbing centers. The location of the peaks of the absorption bands are indicated by the arrows.

irradiation in the R_1 band of NaCl.⁶ It should be noted that both the R_1 and R_2 bands are bleached, that the M , N_1 , and N_2 bands are all bleached somewhat, that no change can be attributed specifically to the F band, that bands grow at 3950, 4800, and 6350 Å and bleach at 3600 and 4300 Å. Irradiation with auxiliary light of wavelength longer than the M band produces qualitatively similar results. Figure 3 gives the results when the crystal was irradiated at 77°K and 4°K in the N_2 band.⁷ Note that this irradiation at about 9200 Å produces marked changes in the 4000 Å region. The change in the number of centers at the peaks was approximately 10% of the number initially present.

Somewhat different results were obtained when the auxiliary light consisted of F -band light.⁸ Here a distinct temporary bleaching of the F band occurred which was about three times as great at 77°K as at 4°K. No change occurred at the peak of the R_1 and R_2 bands although a band seemed to grow between them at 5700 Å. Bands at 3600 and 6300 Å grew while the M , N_1 , and N_2 bands were bleached somewhat by this irradiation.

Results qualitatively similar to Figs. 2 and 3 were found for irradiations with auxiliary dc light lying in the M band, the R_2 band, and at 6350 Å. Little change was produced in the M -band region with the R -band light sources, however. It was not possible to irradiate exclusively into the N_1 band.

Semiquantitative measurements were made of the time delay involved in the temporary bleaching experiment. It was found that the buildup of the change in absorption was appreciably faster than the decay of that change. The time constant for decay was approximately four seconds and was the same at 77 and 4°K. Likewise, this time constant was independent of the wavelength being examined or the wavelength of the auxiliary light.

The data of Figs. 2 and 3 indicate that the previous argument of Lambe and Compton against the model of the R centers of Herman, Wallis, and Wallis is not valid. The change in the two R bands should be about the same with irradiation in either the R_1 or R_2 bands, if the simple model that both R bands arise from transitions in the same center is valid. However, it is clear that a simple model of isolated centers cannot be applied. One is almost required to assume that the M , R_1 , R_2 , and N centers are close together in order to provide a mechanism of interaction between centers that absorb at 1.35 eV but influence centers that absorb at energies as high as 3.4 eV. It seems necessary to conclude, then,

⁶ The auxiliary light filter consisted of Corning glass filters 5120, 3484, and 4303 and a water cell. The combination had an optical density of 0.82 at 5480 Å and 2.0 at 5300 and 5680 Å.

⁷ The auxiliary light filter consisted of Corning glass filters 2540 and 2600 and a water cell. The combination has an optical density of 1.15 at 9200 Å and 2.0 at 8350 Å. The combination did not cut off on the infrared side until beyond 1.1 micron.

⁸ The auxiliary light filter consisted of Corning glass filters 9788 and 5543 and a water cell. The combination had an optical density of 0.34 at 4200 Å and 2.0 at 3500 and 5100 Å.

that this experiment does not allow one to choose between the two models of the R centers that have been proposed.

Polarization of Luminescence

The determination of the symmetry of a color center by the measurement of the degree of polarization of luminescence is meaningful only if it is certain that the excitation and emission occur in the same center, i.e., that energy is not transferred to some other center before the luminescent process occurs. Measurements of the R centers have indicated that excitation in either center gives the same emission band and that the degree of polarization of the luminescence is the same for excitation in either band and is much less than would be expected for a simple dipole.^{3,4} The conclusion that the M , R_1 , R_2 , and N centers are located near others suggests that the above results may be explained in terms of the presence of other centers.

In NaCl, the emission that is excited with R_1 - or R_2 -band light peaks at 1.19 microns and has a half-width of 0.207 eV. This is appreciably different from the 1.07-micron emission of the M center. However, the emission from the N centers has not been reported. It was found that excitation with N_1 -band light gives an emission peak at 1.16 micron with a half-width of 0.28 eV. The present experimental arrangement could not be used to measure the N_2 -center emission. Thus, one can say that the emission with R -band excitation does not coincide with that of the M or N_1 center, but it is not possible to say whether it coincides with the N_2 center. However, it seems unlikely that the R and N_2 centers have the same emission, for excitation spectra show much less excitation in either of the N bands than in the R bands.

The polarization of the luminescence of the R -center emission was measured in several samples of KCl and NaCl at temperatures near 4°K in the hope that better results might be obtained at the lower temperature. It was found that the degree of polarization was the same for R_1 or R_2 excitation and was about the same at 4°K as at 77°K in any given sample. However, the degree of polarization varied among samples that contained different amounts of R and N bands. The values of the degree of polarization P varied between 0.10 and -0.03 for excitation with light polarized along [100] and between 0.28 and 0.08 for excitation with light polarized along [110]. The negative values of P_{100} were found predominantly at 4°K.

The variation in these values of polarization from crystal to crystal implies that the degree of polarization says little about the symmetry of the R center. These variations may result from the influence of other nearby centers, either as a result of lattice distortions, electric fields, or the like, or they may result from the transfer of energy from the R center to other centers making the polarization characteristic of the transfer process more than of the center. Variations among crystals

probably account for the different values of polarization of R emission published by Lambe and Compton⁸ and van Doorn.⁴

A measure of the polarization of the emission excited by N_1 -band light was made in NaCl at 4°K. It was found that

$$P_{110}=0.40 \quad \text{and} \quad P_{100}=0.17.$$

Although the center cannot be represented by a simple dipole, the above results indicate that the symmetry axis of the center is along (110).

Interaction of the M Center with the Lattice

The nature of the interaction of the M center with the lattice can be deduced from measurement of the variation of the half-width of the absorption bands as a function of temperature. Although a complete investigation of this was not made, the half-width at room temperature and at 77°K can be used to get an estimate of the vibrational frequency ν_0 that influence the center in its ground state.⁹ These half-widths were 0.182 and 0.096 eV, respectively. The value of ν_0 was found to be 1.7×10^{12} cps for NaCl. This number is appreciably less than 7.8×10^{12} cps, the longitudinal optical vibrational frequency of the lattice. It can be concluded, then, that the ground state of the M center is primarily influenced by local interactions and not by interactions with the entire lattice. The value of ν_0 for the F center— 4.4×10^{12} cps—is appreciably greater than the value found for the M center in NaCl. Thus, the local interaction is appreciably different in the two centers—a result that would be expected from the dissimilar nature of the two centers.

An examination of the half-widths of the M -center emission peak at room temperature and 77°K gives half-widths of 0.273 eV and 0.172 eV, respectively. The vibrational frequency ν_e that influences the center in the excited state was found to be 4.6×10^{12} cps.

Pekar¹⁰ and Huang and Rhys¹¹ have considered the interaction of the F center with the vibrational phonons of the lattice at large distances from the center. In this treatment the F center is considered to be in a continuous dielectric medium. The absorption of a photon

excites the F center and simultaneously produces phonons at a large distance from the center. Thus, there is no relaxation of the lattice near the center after the absorption process. On this model it is expected that the absorption and emission bands will have the same half-widths. The experimental results show that the emission band is appreciably wider than the absorption band in the M center. This is further evidence that the center is predominantly influenced by local interactions with the neighboring atoms.

DISCUSSION

The above results on the temporary bleaching effect indicate clearly that the R_1 , R_2 , M , N_1 , and N_2 bands are affected by irradiation into the R_1 , R_2 , M , or N_2 bands. Since irradiation into the long-wavelength bands influences the short-wavelength bands, it is concluded that the centers responsible for these bands are not isolated from each other. The close proximity of all of these centers with the resultant interactions among them is such a complicated situation that arguments using these data are not conclusive in indicating whether the R_1 and R_2 bands arise from two isolated centers as suggested by Seitz or whether both R bands arise from transitions in the same center as suggested by Herman, Wallis, and Wallis.

The symmetry of the R_1 and R_2 centers does not appear to be firmly established since the degree of polarization of the luminescence seems to be a function of the presence of other centers. Thus, it is not possible at this time to say whether the models of the R centers have the correct symmetry.

In contrast to the R centers, the M center appears to be rather well understood. The symmetry of the model¹—an electron trapped at a complex of two negative- and one positive-ion vacancies—agrees with that observed for the center,^{3,4,12} the properties of the center appear to be determined predominantly by the local interactions with the lattice, and the theoretical calculations¹³ give transition energies that are in reasonable agreement with the observed location of the M band. However, transitions to the second excited state have not been observed experimentally although they are predicted by the theory to have appreciable oscillator strengths.

⁹ See reference 5 for a complete discussion of this type of measurement as applied to the F center.

¹⁰ S. I. Pekar, J. Exptl. Theoret. Phys. (USSR) **20**, 510 (1950); **22**, 641 (1952).

¹¹ K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

¹² M. Ueta, J. Phys. Soc. Japan **7**, 107 (1952).

¹³ Inui, Uemura, and Toyogawa, Progr. Theoret. Phys. Japan **8**, 355 (1952); B. Gourary and P. Luke, Phys. Rev. **107**, 960 (1957) and **108**, 1647 (1957).