this is not small. Although s.o. interaction falls off faster in the heavier alkalis, neglect of the surface terms cannot be justified for them without further examination.

It is to be noticed that the shift just found arises from the difference between the operators X, Y and x, y. Thus an electron at $\mathbf{k}=0$ in an s band can exhibit a g shift orders of magnitude larger than when in the same atom in the isolated state.

The estimate just given of the various terms of (22) summarizes the results of this calculation. In closing, it is perhaps worth while to remind oneself that there is no reason why the contributions of the higher orders in k should be insignificant. It is also important not to forget the limitations of the one-electron approximation. In the present problem it is the interaction with the core electrons (polarization, exchange) which is most likely to affect the result rather than the interaction between conduction electrons.

ACKNOWLEDGMENTS

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Luminescence and Symmetry Properties of Color Centers*

JOHN LAMBE AND W. DALE COMPTON
United States Naval Research Laboratory, Washington, D. C.

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A study has been made of the luminescent emission of F, M, and R centers in NaCl, KCl, and LiF. When such centers are excited by polarized light, the resulting emission can be analyzed for polarization. This yields information on the symmetry properties of the emitting center. In the case of M centers and of F centers made at 77°K the results obtained are consistent with the models widely used for these centers.

In the case of the R_1 and R_2 centers the situation is more complex and it appears that as far as optical properties are concerned some relationship exists between these centers. Excitation in either band yields the same emission band with very similar polarization properties. This has been interpreted in terms of an energy transfer process between R_1 and R_2 centers.

When crystals containing F, M, and R centers are investigated, the behavior of the F-band emission is markedly changed from the case where only F centers are present. The characteristic F-center emission disappears and instead F-band excitation gives the emissions characteristic of either the R_1 or M centers. Under these conditions the emission excited by polarized F-band light is polarized. Experiments were conducted to test whether these effects might be ascribable to the presence of "higher" excited states of the M and R centers in the region of the F band. This does not appear to be the case. It is therefore concluded that energy transfer processes can occur between the F center and the M and R centers. The observed dichrosim of the F band is ascribed to an interaction of F centers with nearby M and R_1 centers.

INTRODUCTION

SEVERAL experiments have been reported in recent years that deal with the symmetry properties of M centers in KCl. The work of Ueta[1] clearly demonstrated the anisotropic nature of the M center. This was done by bleaching in the M band with polarized light. This had the effect of removing M centers whose major absorption was along the direction of polarization while leaving behind M centers whose major absorption was in a different direction. Ueta was then able to observe a dichrosim in the M-band absorption. This anisotropy of the M center was also demonstrated in the work of van Doorn and Haven.[2] In their work a reorientation of M centers was induced by irradiation with polarized F-band light. They then found that both the M- and F-band absorptions were dichroic.

Another type of experiment which deals with the symmetry properties of color centers has been reported by Feofilov[3] on NaF and LiF. Feofilov utilized the emission of color centers to obtain information on their symmetry properties. This method is based upon the idea that an anisotropic absorber should be an anisotropic emitter. Thus excitation of such centers with polarized light leads to emission that is polarized. By studying the relation between polarization of the excitation and emission one can determine some of the symmetry properties of the emitter.

In the present work we have essentially utilized the technique of Feofilov and extended it to study two types of problems. The first part is a study of individual centers in KCl and NaCl; namely, the F, M, R_1, and R_2 centers. The second part is a study of interactions between these various centers.

In order to carry out the above program it was first necessary to study the M- and R-center luminescence, since no information was available on this aspect of

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* This work was presented in part at the Color Center Symposium, Argonne National Laboratory (October, 1956).

[1] M. Ueta, J. Phys. Soc. Japan 7, 107 (1952).

[2] C. Z. van Doorn and Y. Haven, Phys. Rev. 100, 753 (1955).

[3] P. P. Feofilov, Doklady Akad. Nauk 92, 743 (1953).

these centers in NaCl and KCl. A study of spectral emission and excitation properties was therefore carried out in the course of this work.

EXPERIMENTAL METHODS

Since several different experiments were carried out, important experimental details will be noted in the sections to which they apply. In general, however, the experiments consisted of a study of excitation spectra, emission spectra, and polarization of emission and absorption.

Emission spectra were made using a quartz prism monochromator and either an RCA 6217 photomultiplier or a lead sulfide cell detector depending upon the spectral location of the emission. Excitation spectra were made with a grating monochromator using a tungsten lamp, mercury lamp, or hydrogen lamp, again depending on the spectra being studied.

Polarization studies were made with the apparatus shown in Fig. 1. This permitted excitation of the crystals with polarized light and the measurement of the polarization of the emission. The data obtained in this way will be given in terms of a parameter P, the degree of polarization. To obtain P, the emission intensity was measured with the analyzer parallel to the polarizer (I_1), and then with the axis of the analyzer crossed with respect to the polarizer (I_2). Then P is defined by

$$P=(I_1-I_2)/(I_1+I_2).$$

Thus P is a positive number when the maxima in the emission and excitation are parallel, but negative when these two maxima are crossed. In case of unpolarized emission P is equal to zero. All of these cases are encountered in this work.

Synthetic crystals of LiF, NaCl, and KCl were obtained from Harshaw Chemical Company. Natural NaCl crystals from Baden, Germany,[4] were also used. Most of the work here was done on crystals in which F, M, R_1, and R_2 centers had been produced by irradiation with 2-Mev electrons. Some work was also done on additively colored KCl, but no essential differences were found between the radiation-damaged KCl and the additively colored material.

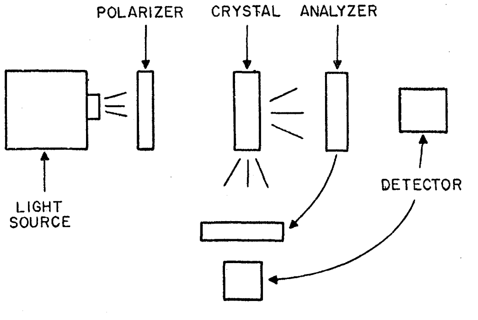

FIG. 1. Apparatus used for studying polarization of emission. Crystal could be kept at room temperature or liquid nitrogen temperature.

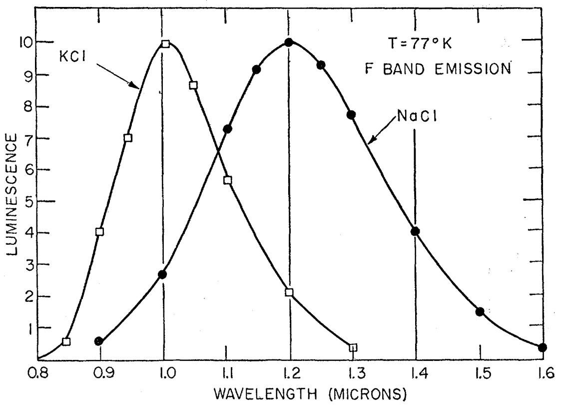

FIG. 2. F-band emission spectra for KCl and NaCl. These crystals were colored by high energy irradiation at 77°K and kept at 77°K until emission spectra were taken. No M or R centers were present in these crystals. The ordinate, the number of quanta emitted per unit wavelength, is not corrected for changes in dispersion of the quartz prism monochromator.

I. PROPERTIES OF CENTERS

Experimental Results

A. F Centers

Consider first the F center and its emission. In order to observe the true emission of F centers, the crystals must be prepared in special ways. This is evident from previous studies which have been reported.[5] In the present work F centers were made in KCl and NaCl by bombarding these crystals with 2-Mev electrons at 77°K. The crystals were then maintained at 77°K until the study of their luminescence had been made.

Measurements were made of the emission spectra of these crystals when they were excited by F-band light. These are shown in Fig. 2. The emission peak is at 1.01 μ for KCl and 1.20 μ for NaCl. The results for KCl are in agreement with results reported for additively colored KCl made by quenching the crystals from high temperatures to liquid nitrogen temperature and then measuring at 77°K. For NaCl, previously reported results[5] were not consistent. This probably resulted from the difficulty in obtaining additively colored NaCl crystals that contained only F centers.

Excitation spectra were also taken and are shown in Fig. 3. These spectra show that the emission is indeed due to F-band excitation.

As a check on results to be cited later, measurements were made on possible polarization effects of the F-band emission when excited by polarized light. No polarization was found. This is reasonable for F centers, since

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[4] Natural sodium chloride crystals from Germany were made available by the Smithsonian Institution, Washington, D. C. (Sample Catalog No. 62946).

[5] Botden, van Doorn, and Haven, Philips Research Repts. 9, 469 (1954).

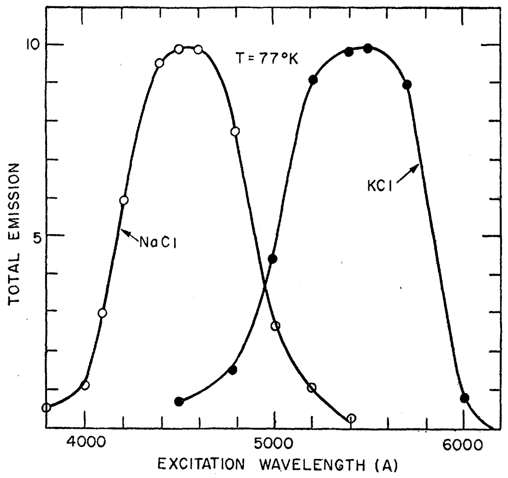

FIG. 3. Excitation spectra for F-band emission. These were the same crystals as used for the measurements of Fig. 2.

they have cubic symmetry. Thus, F centers made at 77°K and kept at that temperature behave as one would expect. It must be noted that no M or R centers were present in these crystals.

The efficiency of F-center emission was not accurately determined, but it appeared to be at least of the order of 10%.

B. M Centers

We now discuss crystals which contain not only F centers, but also M, R_1, and R_2 centers. Such crystals were made by subjecting KCl, NaCl, and LiF to 2-Mev electron bombardment at 300°K. In this section we shall consider the M center.

M-center emission has been reported to be at 6700 A for LiF.[6] Emission peaks were found at 1.08 μ for KCl and 1.07 μ for NaCl when these crystals were excited in their respective M bands at 77°K. Figures 4 and 5 show these emissions. Excitation spectra are shown in Figs. 6 and 7. These show a peak corresponding to the M band in each material.

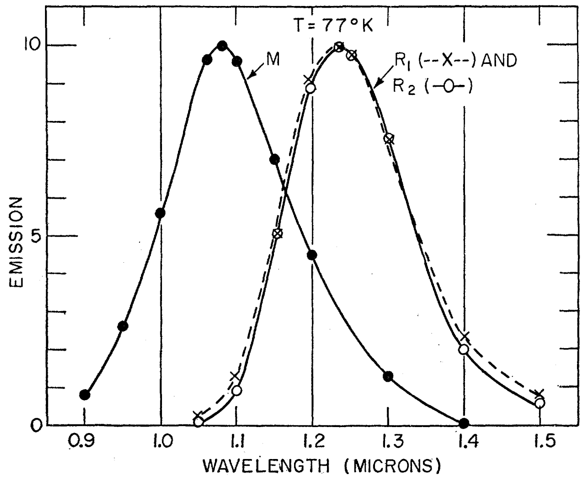

FIG. 4. Emission spectra for M, R_1, and R_2 centers in KCl at 77°K. The crystal was colored by high-energy irradiation at 300°K.

Polarization measurements were made on all of these crystals at 300°K and 77°K. For comparison with theory[7] the polarization of the emission was measured as follows. Light was incident on the (100) face of the crystal. This light was polarized, first, in the [011] direction and then in the [001] direction. The polarization of the emission was then analyzed for each of these polarizations of exciting light. The emission was observed with the detector located on the [100] axis. In Table I is shown the ratio of emission intensities observed as the analyzer was rotated. In each case the maximum in the emission was parallel to the direction of the polarization of the exciting light.

No strong temperature dependence was found for M-band emission, and no changes in polarization could be found as a function of temperature between 300°K and 77°K.

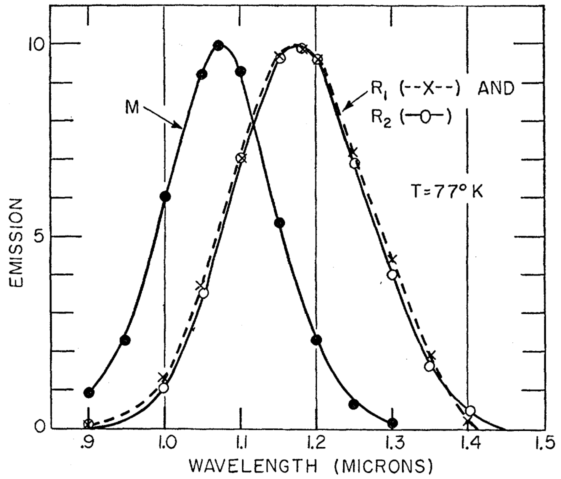

FIG. 5. Emission spectra for M, R_1, and R_2 centers in NaCl at 77°K. The crystal was colored by high-energy irradiation at 300°K.

C. R_1 Centers

The R_1-band emission was studied in KCl and NaCl. This emission peaks at 1.24 μ for KCl and 1.18 μ for NaCl as shown in Figs. 4 and 5. Its intensity was much less at 300°K than 77°K so that all measurements were made at 77°K. Figures 6 and 7 show the peak in excitation spectra corresponding to the R_1 band in KCl and NaCl, respectively.

Polarization measurements were carried out as for the M center. The results are shown in Table II. When the exciting light was polarized along the [001] direction, the emission showed such a small polarization that the value reported is quite uncertain and could be in error by nearly a factor of 2.

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[6] C. C. Klick, Phys. Rev. **79**, 894 (1950).

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

D. R_2 Centers

In KCl and NaCl, the emission properties of the R_2 center were so similar to the R_1 center that one could not distinguish between R_1- and R_2-center emission. These emission spectra are shown in Figs. 4 and 5. Excitation spectra are shown in Figs. 6 and 7. These clearly show a peak corresponding to the R_2 band. The efficiency of R_2-emission was also much lower at 300°K than at 77°K.

Polarization measurements were made, and the results are shown in Table III. These results are also essentially the same as the data given for the R_1 center.

Discussion

A. F Centers

The results reported here indicate that F centers that have been made at 77°K by high-energy irradiation give efficient isotropic emission. For KCl, at least, the results are in good agreement with emission obtained from additively colored crystals. The value of efficiency reported here is only approximate, but it appears to be appreciable. This is consistent with the work of Becker[8] on KCl, where accurate measurement of efficiency on additively colored KCl yielded efficiencies of about 50%.

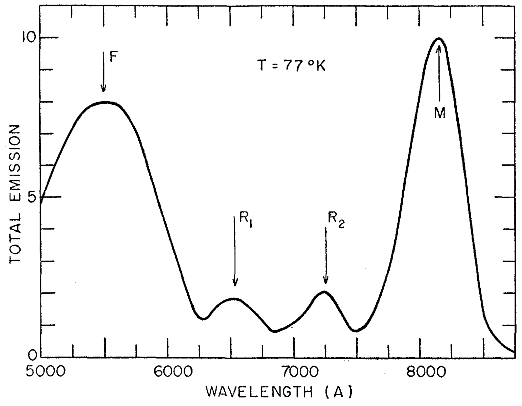

FIG. 6. Excitation spectra for emission at 77°K from KCl crystal containing F, M, R_1, and R_2 centers.

B. M Centers

The results on the M center will be considered in terms of the model that Seitz[7] proposed for this center. On this model, the M center is represented as an electron trapped at a site consisting of two negative ion vacancies with an adjacent positive ion vacancy. On the basis of wave functions that have been used in energy calculations,[9] the M center is represented by a simple dipole oscillator whose optical absorption properties give rise to the M-band absorption. This dipole is oriented along the line joining the two negative ion vacancies, that is along a line corresponding to a face diagonal. A crystal containing M centers will thus have an array of such dipoles oriented along various face diagonals, of which there are six independent possible orientations. If such an array is excited with polarized light, one can easily compute the degree of polarization that would be expected in the emission. Such calculations were made and are also shown in Table I along with the experimental results.

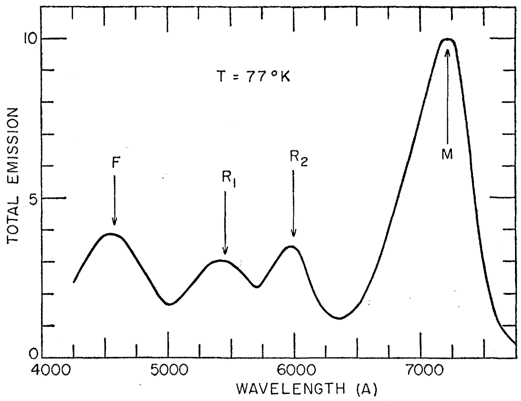

FIG. 7. Excitation spectra for emission at 77°K from NaCl crystal containing F, M, R_1, and R_2 centers.

The agreement between the computed and observed degree of polarization is reasonably good. These results imply that any M-center model that does not have a face diagonal as an axis of symmetry is not possible. This agrees with the conclusion reached by Ueta[1] and van Doorn and Haven[2] from absorption measurements. From these results, however, one can only confirm the expected symmetry of the M center. Specific details, such as the existence of the neighboring positive-ion vacancy, cannot be deduced from these observed symmetry properties. The measurements reported here do indicate, however, that the M center can be represented with a good degree of accuracy as a simple optical dipole oriented along a face diagonal.

C. R_1 and R_2 Centers

The results obtained for these centers will also be discussed in terms of the models that Seitz[7] suggested

TABLE I. The observed degree of polarization of M-band emission for M-band excitation. The M-band exciting light was polarized first along [011] and then along [001]. The bottom line shows the degree of polarization expected on the basis of Seitz's[a] model for this center.

	[011]	[001]
KCl	+0.60±0.02	+0.33±0.02
NaCl	+0.60±0.02	+0.33±0.02
LiF	+0.60±0.02	+0.33±0.02
Calculated	+0.66	+0.33

[a] See reference 7.

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[8] K. Becker and H. Pick, Nachr. Akad. Wiss. Göttingen, p. 7 (1956).

[9] Inui, Uemura, and Toyozawa, Progr. Theoret. Phys. (Japan) 8, 355 (1952).

TABLE II. The observed degree of polarization of R_1-band emission for R_1-band excitation. The R_1-band exciting light was polarized first along [011] and then along [001]. The bottom line shows the degree of polarization expected on the basis of Seitz's[a] model for this center.

	[011]	[001]
KCl	+0.20±0.02	+0.02±0.01
NaCl	+0.20±0.02	+0.02±0.01
Calculated	+0.66	+0.33

[a] See reference 7.

for them. The R_1 center is represented as an electron trapped at a pair of negative-ion vacancies. The R_2 center is made up of two electrons trapped at a pair of negative-ion vacancies. Just as for the M center, theoretical considerations indicate that the lowest energy optical dipole transition for the R centers should lie along the face diagonal connecting the two negative ion vacancies. Thus, the same calculations should apply to the polarization of the emission. In fact, it must be noted that from a theoretical basis, the models for the R_1, R_2, and M centers should all give the same polarization, and thus polarization measurements cannot distinguish between these various models.

Examination of the experimental results show that the R_1 and R_2 centers are quite different than the M centers. The results indicate that the R_1 and R_2 centers have a twofold axis of symmetry (i.e., a face-diagonal axis) and to this extent the results agree with the proposed models. However, the emission shows much lower polarization than expected. The reason for this small degree of polarization is not known, but it appears that the simple theoretical considerations presented here do not afford an adequate basis for describing the behavior of these centers.

The striking similarity between the behavior of the R_1 and R_2 centers is particularly interesting. Both show essentially the same emission and degree of polarization. This warrants further consideration and will be examined in Part II.

Note added in proof.—While this paper was in press, excitation and emission measurements on NaCl and KCl were published by van Doorn and Haven. [C. Z. van Doorn and Y. Haven, Philips Research Repts. **11**, 479 (1956).] The results of this paper are in substantial agreement with theirs on KCl, but disagree on NaCl. The conclusions presented by van Doorn and Haven are not in agreement with those of this paper.

TABLE III. The observed degree of polarization of emission excited by R_2-band excitation. The R_2-band exciting light was polarized first along [011] and then along [001]. The bottom line shows the degree of polarization expected on the basis of Seitz's[a] model for this center.

	[011]	[001]
KCl	+0.20±0.02	+0.02±0.01
NaCl	+0.20±0.02	+0.02±0.01
Calculated	+0.66	+0.33

[a] See reference 7.

II. INTERACTION BETWEEN DIFFERENT CENTERS

A. R_1- and R_2-Center Interaction

Experimental Results

In view of the similarity between the emission properties of R_1 and R_2 centers noted in Part I, experiments were carried out to investigate the significance of this fact. The principal experiments were based on a property of the R_1 band that was found in the course of this work. It was found that in NaCl at 77°K the R_1 band displayed a temporary instability under the action of fairly intense R_1-band light. Specifically, if one measures the absorption of the R_1 band, it is found that this absorption can be decreased by intense R_1-band excitation. This effect might be termed a temporary bleaching. The experimental setup used to detect this effect is shown in Fig. 8. The light used for measuring the absorption is chopped at 10 cps and the detector is tuned for this frequency. This permits the use of a steady auxiliary light without affecting the absorption measurement. The results are shown in Fig. 9. It is noted the R_1-band absorption, as measured at 5450 A, decreases immediately upon application of the auxiliary source, and regains its former value when the auxiliary light is removed. A measurement was made of absorption at different wavelengths in the R_1-band region and it was found that it was indeed the R_1 band that was decreased and not, for example, an effect due to the tail of the F band under the R_1 band.

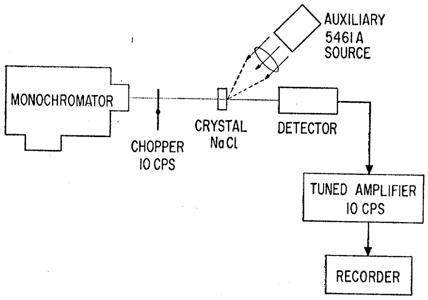

FIG. 8. Apparatus used to detect bleaching effects on R_1 band in NaCl. Crystal was at 77°K.

Absorption measurements were also made of the absorption in the R_2 band at 6100 A and also of the R_1- and R_2-band emission. The results are shown in Fig. 9. It is seen that, although there is a temporary reduction in the R_1-band absorption, the R_2-band absorption is unaffected. However, the emissions due to R_1-band excitation and R_2-band excitation both decrease with the application of auxiliary R_1-band light.

A similar experiment was carried out with an auxiliary source that gave light in the R_2 band rather than the R_1 band. This was done by filtering a tungsten lamp to give light in a band around 6100 A with essentially no light of wavelength shorter than 6000 A or longer than 6500 A. When the crystal was irradiated with such light a decrease in R_1 absorption (5450 A) was found, but R_2 absorption (at 6100 A) did not decrease. If the auxiliary light was filtered to give light outside of the R_1- and R_2-band absorption regions no decrease of the R_1 band was found. A decrease in the emission of the R_1 and R_2 centers was found when the auxiliary R_2 light was turned on.

Thus, it was found that a temporary decrease in the R_1-band absorption could be induced by irradiation in the R_1 or R_2 bands, that the R_2-band absorption was unaffected by irradiation in the R_1 or R_2 bands, and that the emission of the R_1 or R_2 centers was decreased by irradiation in either the R_1 or R_2 bands.

Discussion

It appears that some interaction or relationship exists between the R_1 and R_2 center. The first point to be considered is the similarity of emission properties. Why should two different centers yield emissions that are identical within experimental error? A simple answer to such a question is that only one center exists here and that the two absorption bands represent two different excited states of the same center.[10] On this basis the R_2 band would represent a transition to a first excited state and the R_1 band a transition to a second excited state. However, the emission in both cases would be assigned to a transition from the first excited state to the ground state. This viewpoint, though attractive, is not consistent with the observed polarization effect. On the basis of the wave functions used in discussing this model[10] the second excited state absorption should be represented by two dipoles that are perpendicular to each other and to the dipole representing the first excited state absorption. Thus, the emission would be from a dipole at right angles to the absorbing dipoles. An analysis of this situation shows that the degree of polarization of the emission would be negative for excitation polarized along [011]. Thus it appears that the R_1-band absorption cannot be interpreted as an excited state of a center that has the R_2 band as its first excited state, at least on the basis of a simple picture. Since these arguments may depend somewhat on specific details, it will be shown that the experiments on R_1 band instability are consistent with this conclusion.

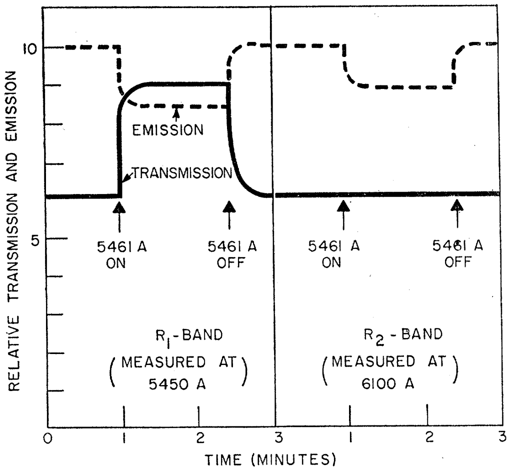

FIG. 9. Effect of intense auxiliary R_1 band light (5461 A) on the transmission and emission of the R_1 band and R_2 band in NaCl at 77°K.

Is is noted from the results in Fig. 9, that R_1-band absorption can be decreased while R_2-band absorption remains unchanged. Presumably the reduction in the R_1 band is due to a reduction in the number of centers responsible for this absorption. Thus, if the R_1 and R_2 absorptions arise from the same center, a reduction in R_2 absorption must accompany any reduction in R_1 absorption. Since this is not the case, it appears that an interpretation based on first and second excited states is not consistent with these observations.

An alternative explanation of the similarity of R_1 and R_2 emissions is that energy transfer can occur between these two centers. In this case, energy absorbed by an R_2 center could transfer to an R_1 center with the resulting emission being the same as if the R_1 center had been excited directly. If the R_2 center transfers its energy to the R_1 center, then the emission with either R_1 or R_2 excitation should decrease if the number of emitters (R_1 centers) is lowered while the number of R_2 centers is left unchanged. This is seen to be the result of Fig. 9.

It is also of interest to note that intense irradiation in the R_2 band induced a temporary reduction in the R_1 band. This is also consistent with the view that energy can be transferred from R_2 to R_1 centers.

Since we are led to postulate an energy transfer, the question arises as to the nature of such a process. One possibility is that a form of resonant transfer or sensitized luminescence occurs. Such processes have been studied experimentally and theoretically for numerous systems. Actually it seems unusual that a center such as the R_2 center could transfer energy to a center whose principal absorption lies at higher energy. It is likely, however, that the tail of the R_1 band extends into the R_2 band sufficiently to make resonant transfer possible. Thus the R_2 band would excite the R_1 centers at energies lower than the absorption peak of the R_1 band. Until more experimental information is available, more specific explanations cannot be given. For example, it is not established that the R_1 and R_2 centers are really randomly distributed with respect to each other. If some association should exist between these centers the possibilities of transfer might be greatly enhanced. In this connection the work of Herman, Wallis, and Wallis[10] is of special interest since it emphasizes that the ratio

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[10] Herman, Wallis, and Wallis, Phys. Rev. **103**, 87 (1956).

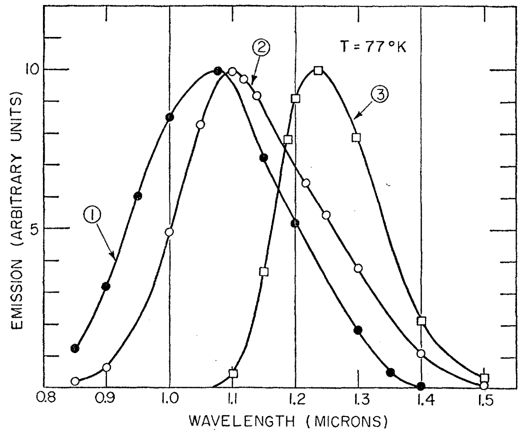

FIG. 10. Emission spectra obtained when KCl crystals containing varying amounts of F, M, and R centers were excited in the F band at 77°K. Crystal for curve 1 contained only F and M centers. Crystal for curve 2 contained more M centers and some R centers. Crystal for curve 3 had a much higher concentration of R centers.

of absorption of the R_1 to the R_2 is nearly constant over a wide range of absorption. Their interpretation was based on first and second excited states of the same center but one might also imply a close association between R_1 and R_2 centers without one actually being a higher excited state of the other.

In addition to the above observations it may be worthwhile to discuss briefly what we have termed the instability of the R_1 center in NaCl. Such an effect could be due simply to the ejection of electrons from R_1 centers and their subsequent return to the R_1 centers after the removal of the bleaching light. This requires that about 10^{14} electrons/cc be "stored" temporarily in some manner. Furthermore, when the R_1 band was reduced by the intense auxiliary light, it was noted that the optical absorption in the F band increased. It is possible that the R_1 center is broken up into an F center and next nearest neighbor anion vacancy and that these can recombine to re-form the original R_1 center. The limited experimental observations presented here are not sufficient to support any firm conclusion on this aspect of the R_1 center.

B. *F*-, M-, and *R*-Center Interaction

Experimental Results

It was emphasized in the section on F centers that the characteristic F-center luminescence was observed only when M or R centers were absent. If this precaution was not maintained, it was found that excitation in the F band gave an emission that was shifted in peak location and was less efficient. It was also found that this new emission was the same as was obtained by exciting directly in the M or R centers.

These effects were particularly studied in KCl. Figure 10 shows the emission resulting from F-band excitation on crystals that contained varying amounts of M and R centers.

The crystals were irradiated with 2-Mev electrons from a Van de Graaff generator at 300°K. A brief irradiation produced F and a few M centers, and the emission (curve 1) at 77°K contained both F- and M-center emission. A longer electron irradiation produced F, M, and a few R centers. The emission at 77°K (curve 2) now contained M- and R-center emission but no F-center emission. A still longer electron bombardment produced F, M, and an appreciable number of R centers. At 77°K the emission was now all R-center emission (curve 3). In all of the above cases the emission at 300°K was only that of the M center.

Weakly x-rayed KCl gave both F- and M-center emission at 77°K. Additively colored KCl that had been quenched to remove all R centers and most M centers also gave a mixture of F- and M-center emission at 77°K. Mixtures of M- and R-center emission with F-band excitation were obtained on electron bombarded NaCl at 77°K. As was reported by Klick,[6] M-center emission was obtained by F-band excitation in x-rayed LiF.

Botden, van Doorn, and Haven[5] have also studied the emission arising from F-band excitation in additively colored alkali halide crystals. They give results on crystals that had been annealed at high temperatures and quenched to 77°K in the dark to remove all M and R centers. The emission was then measured at 77°K. These crystals were then warmed to 300°K and allowed to stand in the dark for a few hours. The emission was then remeasured at 77°K. They found that crystals that had been initially quenched to 77°K gave an emission that agrees with the F-center emission reported here. The emission that was obtained on the crystals

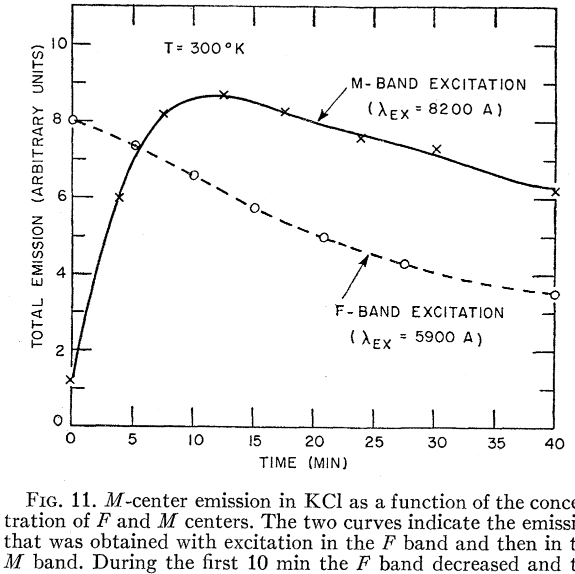

FIG. 11. M-center emission in KCl as a function of the concentration of F and M centers. The two curves indicate the emission that was obtained with excitation in the F band and then in the M band. During the first 10 min the F band decreased and the M band increased. After 12 min both bands decreased. The height of the bands was altered by bleaching with F-band light.

that had stood at 300°K prior to measurement at 77°K agrees with the *M*- and *R*-center emission that we have obtained. Their results, then, are in agreement with those obtained on radiation damaged crystals as reported here.

Thus the coagulation of *F* centers to form *M* or *R* centers reduces the *F*-center emission and produces *M*- or *R*-center emission although the excitation is still in the *F*-band.

Since only the *M* center emits efficiently at 300°K, the study of *F*-band excitation of the *M* center was made at 300°K in KCl by looking at the total emission. Figures 11 and 12 give the results of this study. Figure 11 gives the emission of this crystal as a function of time. One curve is the emission with *F*-band excitation, while the other is the result with *M*-band excitation. The absorption measurements of Fig. 12 were made on the same crystal. Curve 1 was the initial absorption prior to exposure with *F* light. Curve 2 was taken after exposure to *F* light at about the time that the emission for *M* band excitation was a maximum. Curve 3 was taken after the emission measurements were completed. Consider the first 10 min of Figure 11. As the *M*-band absorption increased with time, the emission with *M*-band excitation increased with time while the *M*-band emission with *F*-band excitation decreased with time. Simultaneously the *R* bands had grown. Emission measurements at 77°K showed that the *F* band was now exciting the *R* centers. Thus, it is concluded that *F* light excites *M* centers only if the number of *R* centers is small.

The emission with *F*- or *M*-band excitation decreased with time after the first 12 minutes. By comparing curves 2 and 3 of Fig. 12, it is seen that the *M* band had bleached and thus the emission would be expected to decrease. This does not contribute to the initial drop in emission with *F*-band excitation, for the *M* band grows initially.

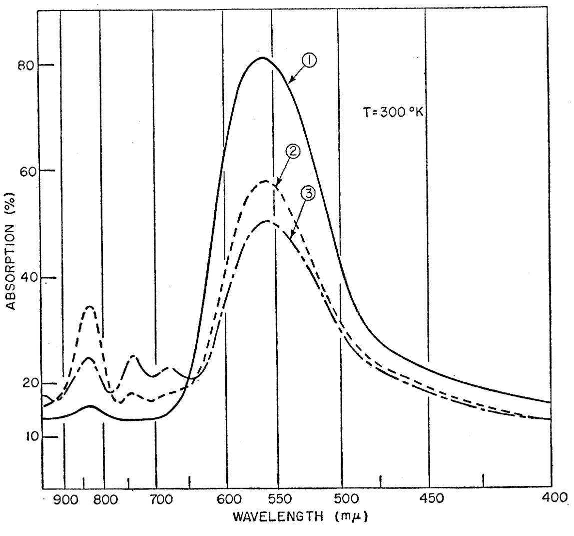

Fig. 12. Absorption curves for a KCl crystal as it was bleached with *F*-band light. Curve 1 is for a freshly colored crystal. Curve 2 after 10 minutes of bleaching. Curve 3 after 40 minutes of bleaching. This was the same crystal as was used for the measurements of Fig. 11.

Table IV. The observed degree of polarization of *M*-center emission excited by *F*-band excitation. The light exciting the *F* band was polarized first along the [011] direction and then along the [001] direction.

	[011]	[001]
KCl	−0.30±0.04	−0.10±0.04
NaCl	−0.30±0.04	−0.10±0.04
LiF	−0.30±0.06	−0.20±0.06

An approximate quantum efficiency measurement for the *F*-band excitation of *M* centers was made for the case of no *R* centers. It was found that the efficiency was a few percent and that this efficiency was essentially temperature independent.

It was previously noted that excitation with polarized *F*-light gave unpolarized emission if *M* or *R* centers were absent. This was interpreted as evidence that such *F* centers are isotropic absorbers and emitters. However, if *M* or *R* centers were present, it was found that excitation with polarized *F* light gave polarized emission. Thus, both the energy and symmetry properties of the emission due to *F*-band excitation are radically altered by the presence of either *M* or *R* centers.

This effect was studied at 300°K in KCl, NaCl, and LiF since *F*-band excitation gave only *M*-center emission at this temperature. The results are given in Table IV for *F* light of two different polarizations. It should be especially noted that the degree of polarization was negative. That is, the plane of polarization for maximum emission was rotated 90° relative to the plane of polarization of the excitation.

An analogous dichroic behavior of the *F* band was observed by van Doorn and Haven.[2] They irradiated additively-colored KCl with *F* light polarized along [011] at 77°K. The absorption of the *F* and *M* bands was then measured with polarized light. They found that the *F* band had a higher absorbance for light that was polarized along $[0\bar{1}1]$ while the *M* band had a higher absorbance for light that was polarized along [011]. This clearly demonstrated that the *F* band can influence the *M* band. It was not possible to induce dichroism in the *M* band by irradiation with polarized *M* light at these temperatures, however.

We have found that polarized *F* light also induces dichroism in the *R* bands. In NaCl this could be produced at either 300°K or 77°K by irradiation with polarized *F* light. A much longer time was required to obtain the effect at 77°K. Figure 13 shows the absorption of the R_1, R_2, and *M* bands in NaCl after a brief irradiation at 300°K with *F*-light polarized along [011]. The resulting *F*-band absorption was less along the [011] direction than along the $[0\bar{1}1]$ direction.

Figure 14 shows the *F*-band absorption spectrum and

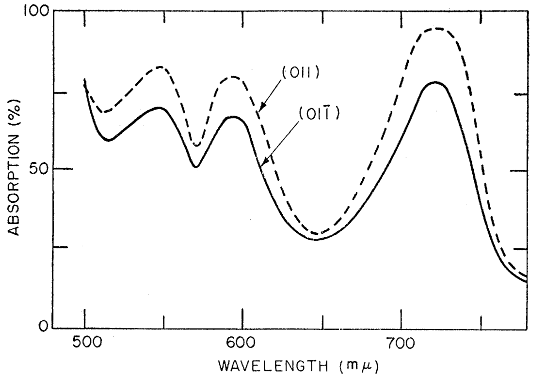

FIG. 13. Absorption of polarized light by an NaCl crystal that had been irradiated at 300°K by F-band light polarized along [011]. The measurement was then made at 77°K. The F band absorption was smaller along [011] than along [0$\bar{1}$1].

the excitation spectrum of M-center emission by F-band light for NaCl at 300°K. Similar data were found for KCl. It should be noted that the F-absorption coincides with the excitation of M-band emission.

Discussion

Five experimental observations have been given that indicate that F, M, and R centers strongly interact. These are: (1) emission characteristic of the F center disappears when an appreciable number of M or R centers are present; (2) if an appreciable number of R centers are present, then F-band excitation gives only R_1-center emission, although the M centers emit their characteristic radiation when excited with M light; (3) the excitation spectrum of M-center luminescence by F-band light and the F-band absorption agree in peak position and half-width; (4) M- and R-center emission is polarized if the F-band excitation is polarized; and (5) dichroic absorption can be introduced in the F, M, and R bands by irradiation in the F band with polarized light.

The nature of the interaction process will now be discussed. One explanation of the above effects is that second excited states of the M and R_1 centers are hidden beneath the F band. The other possibility is that an energy transfer mechanism exists whereby energy absorbed by F centers can be transferred to M and R centers. Thus, we have a problem very similar to that encountered in the case of the R_1 and R_2 centers.

First, the higher excited state explanation will be considered. If it is assumed that the optical dipole moments associated with transitions from the ground state to the first and second excited states of the M centers are at right angles to each other, then the presence of these second excited states hidden beneath the F band could explain the dichroic absorption and emission effects. It should be noted that a calculation has been made for a second excited state of the M center in NaCl.[9] The optical transition to this state can be represented by a dipole oriented along a cubic axis. Thus, it is not possible for these dipoles to produce the observed dichroism between the directions [011] and [0$\bar{1}$1]. However, a third excited state of the M center should exist that could explain observations (4) and (5) above.

As a result of the similarity of the absorption spectrum of the F center and excitation spectrum of M-center luminescence by F light, as shown in Fig. (14), it would be concluded that the F-band absorption and the absorption of the second M-center excited state have the same peak position and nearly the same half-width. These observations were found for both KCl and NaCl. Thus, the F band and the second-excited-state band of the M center must coincide in both NaCl and KCl.

The assumption that excited states of the M and R_1 centers are hidden beneath the F band does not explain the loss of F center emission when these other centers are present in the crystal. For the F centers should absorb a greater fraction of the incident light than any excited states that are small enough to be hidden beneath the F band. Thus, emission characteristic of the F center should always be present.

Perhaps the most serious objection to the second excited state model arises from the observation that as the M-band absorption increases, the emission with M-band excitation increases but the emission with F-band excitation decreases during the initial period of Fig. 11. If the excitation of the M center with F light arises from the absorption of energy by a second excited state of the M center, then one should expect F and M band excitation to vary in the same way. This is not found.

Thus, it is concluded that the above results do not arise from excited states of the M and R_1 centers that are hidden beneath the F band. It is necessary, then, to conclude that an interaction between these centers exists of such a nature that the excited F center transfers

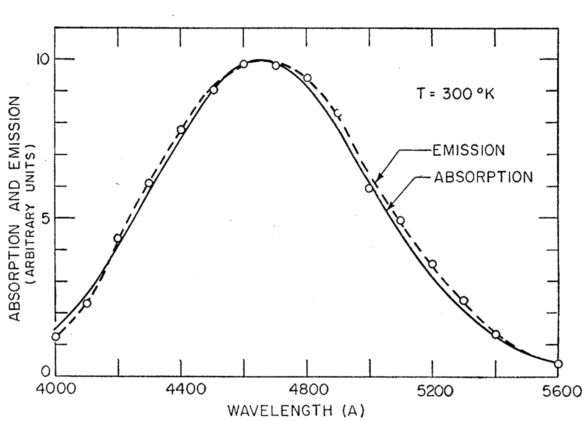

FIG. 14. The excitation spectrum of M-center emission in NaCl. This excitation measurement was confined to the F-band region. The corresponding absorption spectrum is also given. The measurements were made at 300°K. Absorption is in terms of the number of incident quanta absorbed per unit wavelength.

its energy to M or R_1 centers before it relaxes by luminescing.

This transfer process may be a modified resonance transfer or sensitized luminescence process between the F and M or R_1 centers. Consider the F center in NaCl. It absorbs about 2.8 ev and emits about 1.0-ev radiation after a Stokes' shift of about 1.8 ev. This energy is lost to the lattice in a time of the order of 10^{-10} sec. As the F center loses this energy by emitting phonons, it attains an energy equal to that necessary to excite the R_1 center. The F center can transfer its energy to the R_1 center by dipole-dipole interaction if the centers are sufficiently close and if the time during which the centers are in resonance is sufficiently long. It can be estimated that the centers are in resonance for a time of the order of 10^{-11} sec. Thus, the transfer must occur in times of this order. Calculations by Dexter[11] on systems in which dipole-dipole transfer is possible indicates that the two centers involved in the transfer must be quite close if the transfer is to occur in these times. Even if the relaxation time of the center is longer by a factor of 10^3, the range only increases by a factor of 3.

Since the F center becomes resonant with the R_1 center first and then the M center, it is seen that this transfer process can explain the loss of M-center luminescence and the appearance of R_1-center luminescence as the number of R_1 centers increases. According to this model it should transfer to the R_1 center before it can transfer to and excite the M center.

In addition to the transfer of energy, any proposed model must explain such facts as the induced dichroism of the F band. If the F band arises solely from F centers, which have cubic symmetry such an effect can not occur. To explain this dichroism without employing higher excited states, it must be assumed that there is some type of interaction between F, M, and R_1 centers than can impart an anisotropy to the F center. Two possibilities for accomplishing this can be suggested. They are: (1) the action of electric fields on the F center, such as the permanent dipole field of the M center or the monopole field of the R_1 center or; (2) the action of mechanical stresses upon the F center arising from vacancies present in the M and R_1 centers. Such effects would be likely to be of very short range. Thus if the above interactions are to be important, it is essential that the F centers be fairly near the M or R_1 centers, that is within a few lattice sites. If F and M centers are randomly distributed, however, then for the concentrations encountered in this work the average spacing is of the order of 20 lattice spaces apart. Thus if such interaction is to be significant one must assume that F, M, and R_1 centers are not randomly distributed with respect to each other.

As an example of the above points consider an F center located near an M center whose negative ion vacancies lie along the [011] direction. Assume that the F center can transfer energy to this M center. In order to explain the observed polarization of M emission with F excitation and also the induced dichroism, it is necessary that the F center should have a larger absorption for light polarized along the $[0\bar{1}1]$ direction than along the [011]. The major question then is whether an M center can impart such properties to a nearby F center. In order to give a definite answer to this a fairly detailed theoretical analysis of the situation would be required.

It must be noted that the F-band excitation not only excites M-center luminescence, but also can produce a reorientation of M centers at low temperatures. Such reorientation is not produced by direct excitation in the M band at these temperatures.[2] This result cannot be explained in terms of a simple resonance transfer. It is necessary, on the model proposed here, that the M center be able to change its orientation by utilizing the energy that the F center loses by phonon emission, i.e., a local "heating" of the lattice.

Clearly the viewpoint that these so called transfer effects arise from an interaction between centers, rather than hidden excited states, has several complicated aspects. We have therefore stressed the fact that this viewpoint is one which is largely dictated by experiment rather than based on any extensive theoretical considerations. Thus, the description that has been given here is essentially phenomenological.

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[11] D. L. Dexter, J. Chem. Phys. 21, 836 (1953).