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Luminescent Excitation Spectra of F and M Centers in KCl*†

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Luminescent excitation spectra were measured for the F and the M centers in KCl; in particular, for the F center and for two transitions of the M center: the M_1 and M_2 transitions. In all three cases, the excitation spectra were nearly double-Gaussian in shape, and the efficiency for luminescence was nearly independent of the wavelength of the exciting light. A comparison of the dichroic absorption spectrum with the excitation spectrum of the F-band region of crystals with M centers present and oriented provided further evidence for the existence of the M_2 transition proposed by van Doorn and Haven and by Okamoto. The efficiency for luminescence for M centers upon M-band excitation was equal to the efficiency for luminescence for F centers in pulse-annealed crystals of low F-center concentrations. New absorption and luminescent excitation bands in NaF are also reported.

I. INTRODUCTION

THE F center, a point defect in ionic crystals, consists of an electron trapped at a negative-ion vacancy. It has O_h cubic symmetry, in the Schoenflies notation.[1] The F center absorbs light over several ranges of wavelengths, the strongest absorption being in the F band. Weaker absorptions are found at energies greater than that of the F band, namely, in the K, L_1, L_2, and L_3 bands.[2] These absorptions are independent of the polarization of the incident light. The luminescence from F centers upon excitation with light absorbed in any of these bands is unpolarized and isotropic in direction.

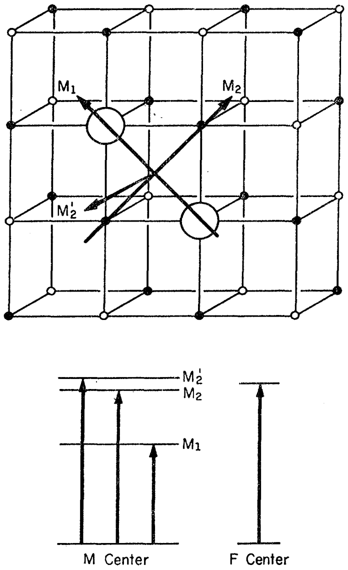

FIG. 1. A single M center imbedded in a NaCl-structure crystal with the main axis on the front surface. The polarizations of the transitions M_1, M_2, and M_2' are indicated and the energies of these transitions are also indicated. The F-center transition energy is given for reference. Symbols: small solid circles, alkali metal ions; small open circles, halogen ions; large open circles, halogen-ion vacancies with one electron trapped at each of them; lines connecting the two large circles, main axis of the M center.

The M center consists of two electrons trapped at two neighboring negative-ion vacancies, as shown in Fig. 1. This center has D_{2h} symmetry. Light of the proper range of energy polarized parallel to the main axis of an M center can excite the center from the ground state to the first excited state, called the M_1 state. This absorption gives rise to the so-called M band. M-band absorption of light by a single M center, or by a group of M centers all aligned with their main axes oriented in the same direction, depends both on the polarization of the incident light, and the direction of propagation of the light. If the M centers are randomly oriented, the M-band absorption is isotropic and independent of the polarization of the incident light. The luminescence from M centers is neither isotropic in polarization nor in direction even for a random orientation of the M centers.[1]

Van Doorn and Haven[3,4] proposed the existence of a second excited state of the M center to account for the direct absorption of light having F-band wavelengths by the M center. Using Okamoto's notation,[5] this is called the M_2 state, with the corresponding absorption being called the M_2 transition. Let us call this the higher-excited M-center states (HES) theory. Referring to Fig. 1, light having F-band wavelengths with the polarization vector perpendicular to the main axis of the M center and parallel to the front surface of the cube will excite the M_2 state. A similar transition in the K-band wavelengths is called the M_3 transition. Light with F-band wavelengths with the polarization vector perpendicular to the front surface of the cube shown will excite the M_2' state; a similar transition in the K-band wavelengths is called the M_3' transition.[5]

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[1] C. Z. van Doorn, Ph.D. thesis, published in Philips Res. Rept. Suppl. No. 4 (1962).

[2] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

[3] C. Z. van Doorn and Y. Haven, Philips Res. Rept. **11**, 479 (1956).

[4] C. Z. van Doorn, Philips Res. Rept. **12**, 309 (1957).

[5] F. Okamoto, Phys. Rev. **124**, 1090 (1961).

Four experimental and theoretical considerations support the HES theory:

First, dichroic absorption spectra were obtained by Okamoto,[5] by van Doorn,[4] and by Delbecq.[6] In these experiments, KCl crystals with both F and M centers present were optically bleached with polarized F-band light to change the orientation of some of the M centers. After this treatment, the absorption spectra for light polarized parallel to and perpendicular to the polarization of the bleaching (or reorienting) light were different, for both the F and M bands. No such dichroism in the absorption occurred if M centers were not present.

Second, the emission spectra upon excitation of KCl and NaCl crystals with F-band light was measured by van Doorn,[4] by Delbecq,[6] and by Lambe and Compton.[7] With F centers but no M centers present in KCl, the emission peak occurred around 1.01–1.04 μ in wavelength. With both F and M centers present, the emission peak shifted to around 1.08 μ, and the half-width of the emission became narrower. The emission peak and shape in this latter case were essentially identical with that found upon M-band excitation. Similar results were found for NaCl.

Third, the polarization of luminescence was determined for excitation of colored KCl crystals with F-band light.[4,6–8] With F centers but with no M centers present, the emission was unpolarized and isotropic in direction. When M centers were introduced into the same crystals, the luminescence upon F-band excitation became nonisotropic in direction and was polarized.

Fourth, theoretical calculations of the energy of several excited states of the M center were made by Meyer and Wood[9] and by van Doorn.[1] Assuming that optical transitions from the ground state to these excited states were allowed, the energy of some of the transitions were about the same as the energy of the F-band transition. The calculations do not, however, agree with the ordering of the dichroic absorption properties of these transitions, as measured by Okamoto.[5]

The above experiments could also be explained by the energy-transfer (ET) theory proposed earlier by Lambe and Compton.[7] In this theory, energy absorbed by the F centers is transferred by Coulomb-dipole interactions to nearby M centers producing excited M centers that relax by luminescing. The F centers, having transferred their energy, can not then luminesce. In turn, the nearness of the M centers to the F centers distorts the symmetry of the F center so that its absorption properties change.

Although most investigators have accepted the HES theory, it is conceivable that the ET theory is correct, or that both theories are correct, with the experimental results being the superposition of the two effects.

In this work, the excitation spectra of the luminescence of the F and M centers in KCl are determined and quantitatively compared with the absorption spectrum of these centers. Measurements were made with crystals containing only F centers and with crystals containing both F and M centers. By proper optical treatment, it was possible to orient the M centers such that only the M_2 transition would absorb light.

If the HES theory is correct, the excitation spectra of the crystal with oriented M centers should have the same spectral shape and position as the absorption data of the M_2 transition, found by dichroic absorption spectra in the F-band region. If the ET theory is correct, the excitation spectra in the F-band region should fit the absorption data for the F band. Thus a comparison of the luminescent excitation spectra with the absorption spectra in the F-band region should give additional evidence of which proposal is correct.

A detailed comparison of the absorption and excitation spectra of the M center, in the M band, and of the F center was also made in order to determine whether the quantum efficiency for luminescence of these centers depends upon the wavelength of the exciting light.

II. EXCITATION-SPECTRUM APPARATUS AND CORRECTIONS TO DATA

Light from a forced-air-cooled Sylvania FAL lamp was focused on the entrance slit of a Bausch & Lomb 250-mm plane-grating (600 grooves/mm) monochromator. Light from the monochromator was focused through filters and polaroids (when used) onto the crystal. The crystal was mounted in a brass Dewar designed for liquid-nitrogen-temperature (LNT) measurements.[10]

The luminescence from this crystal was focused onto a PbS photodetector, through a filter consisting of a Polaroid Corporation XRX-55 sheet, or of a 0.0270-in.-thick slice of polished silicon.

The light reaching the detector was chopped with an aluminum blade at position 1 in Fig. 2, or was polarized with a rotating HR plastic polaroid (obtained from the Polaroid Corporation) at position 2. A reference signal for a lock-in amplifier was generated by this chopper. An amplified signal from the PbS detector was fed into a phase-sensitive lock-in amplifier, tuned to 100 cps. The output of the lock-in amplifier was recorded on a Varian chart recorder.

The experimental excitation spectrum E, the total number of photons in a given energy range emitted per second by the luminescing crystal into a unit solid angle, is of little direct significance because of many factors influencing the results, such as the lamp spec-

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[6] C. J. Delbecq, Z. Physik **171**, 560 (1963).

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

[8] G. Kuwabara and A. Misu, J. Phys. Soc. Japan **13**, 1038 (1958).

[9] A. Meyer and R. F. Wood, Phys. Rev. **133**, A1436 (1964).

[10] The Dewar had four quartz windows, one of which was mounted on a slide so that it could be replaced by a 1-mm-thick beryllium window by sliding the pair of windows on the Dewar without the loss of vacuum. The crystal was mounted on a copper base, which was in good thermal contact with the coolant reservoir. The temperature of the crystal was nominally that of the coolant in the trap.

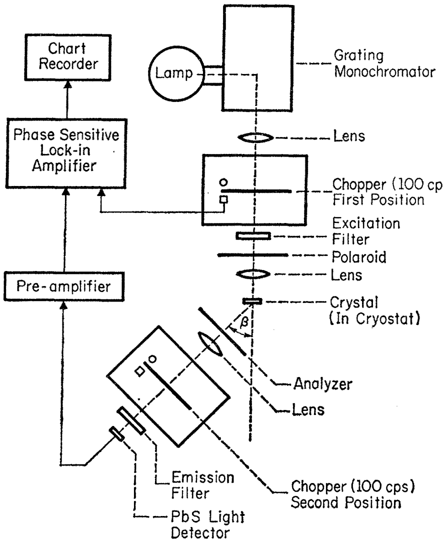

FIG. 2. Apparatus for excitation spectra and polarization of luminescence.

trum, crystal absorption, and optical filters used. A corrected excitation spectrum C can be determined from the experimental excitation spectrum E by

$$C=\sum_i \eta_i\alpha_i=k\frac{\sum_j(\alpha_j x)}{1-\exp[-\sum_l(\alpha_l x)]}D^{-1}E,$$

where α_i is the absorption constant of the ith absorption band at wavelength λ, η_i is the efficiency for luminescence for the center responsible for the ith absorption band, k is a proportionality constant, x is the thickness of the crystal, and D is the number of photons per second per energy interval incident on the crystal. In deriving the above correction formula, it was assumed that α_i was constant throughout the crystal (i.e., the crystal was uniformly colored); reflection losses are constant and small; absorption and emission are isotropic; no reabsorption of the emission occurs; and if energy transfer occurs, it occurs with the same probability throughout the crystal.

The absorption spectrum was determined with a Cary 14R spectrophotometer, with HR or HN32 polaroids mounted in the Cary beams. The number of photons versus wavelength of the exciting light was determined directly using a radiation thermocouple as a detector.

III. DATA ON *F* CENTERS IN KCl

Figure 3 shows the corrected excitation spectrum for several additively colored crystals. The half-widths of three of them agree within 2mμ of each other, while the fourth one is narrower due to nonuniformity of coloration caused during the annealing process.

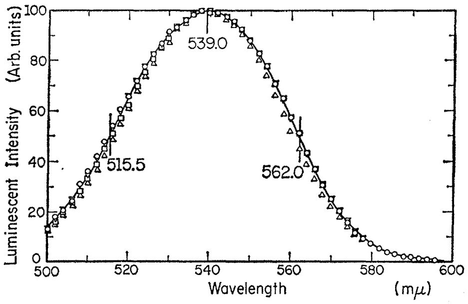

FIG. 3. Corrected excitation spectra of *F* centers in KCl.

Symbol	Sample name	Concentration (centers/cm^3)
○	144C	8.0×10^{16}
△	14D	2.2×10^{17}
▽	54D	4.3×10^{16}
□	78D	4.6×10^{16}

Sample 78D was a Harshaw KCl crystal colored by the van Doorn technique,[1,11] cleaved to 0.973 mm thick, and pulse-annealed at 600°C for 52 sec in the dark, and quenched rapidly in the dark on a heavy clean copper block. The crystal was then mounted in the brass Dewar, using only illumination from a flashlight filtered with a Corning 2030 filter. The absorption spectrum at LNT showed a peak *F*-band absorption of 0.701 o.d. and no *R*, *M*, nor *N* bands. For this concentration of *F* centers, about 4.6×10^{16} centers/cm^3, Miehlich's data[12] suggest that the efficiency for luminescence of the *F* center is 87%. No *R* centers were observed in the excitation spectrum.

In Fig. 4, the absorption and corrected excitation spectra are drawn in Gaussian plots. The data on the low-energy side could not be matched with a single straight line; a single straight line was drawn to fit the

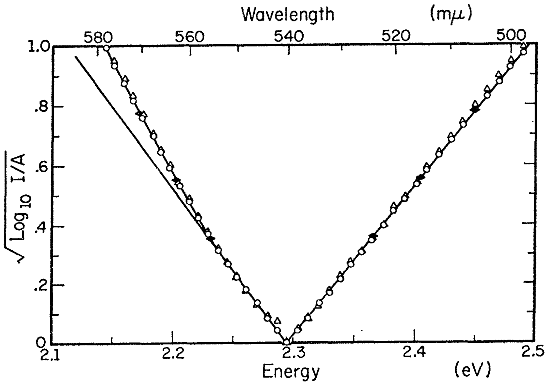

FIG. 4. Gaussian plots for the absorption and corrected excitation spectra of *F* centers at low concentration in KCl, sample 78D.

Symbol	Meaning
○	Absorption spectrum
△	Corrected excitation spectrum
◆	$\frac{3}{4}$-, $\frac{1}{2}$-, and $\frac{1}{4}$-maximum points
A	Height of the spectrum at energy E divided by the peak height

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[11] C. Z. van Doorn, Rev. Sci. Instr. **32**, 755 (1961).
[12] A. Miehlich, Ann. Physik **176**, 168 (1963).

data near the peak, and was extended toward the tail of the band. The remainder of the curve is a nonstraight curve for best fit to the data. Thus the Gaussian fits well on the high-energy side, but only approximately on the low-energy side. Since the absorption and excitation spectra differ at most by only 5% inside the quarter-maximum positions, and by only 2% inside the half-maximum positions, we can conclude that the efficiency for luminescence for F centers at low concentrations in KCl is constant throughout the F-band region, within this accuracy.

Sample 148D, 0.267 mm thick, was colored at LNT for 6 h by x rays, filtered through 0.0066 in. of copper, from a Norelco MG-150 x-ray machine operating at 100 kV and 23 mA. With an F-band absorption of 1.079 o.d. at LNT, or with 2.6×10^{17} centers/cm^3, the F centers would luminesce with an efficiency of 55%, or about $\frac{5}{8}$ of the efficiency of sample 78D.[12] Since the M-band absorption was only 0.008 o.d., the M centers can be neglected compared to the F centers. For the F-band spectra on Gaussian plots, the absorption and excitation spectra practically coincided, and agreed well with the data of the spectra given in Fig. 4 for small concentrations of F centers. Thus the concentration of F centers does not affect the shape or position of the absorption spectrum significantly, in agreement with the work of Konitzer and Markham.[13] Of more significance here, the concentration of F centers does not affect the shape or position of the luminescent excitation spectrum significantly. The results of Miehlich[12] and of Compton and Kabler[14] clearly indicate that the efficiency of luminescence of F centers decreases with increasing concentration of F centers. One might suggest that a resonant transfer of energy from one F center to another nearby F center occurs during the relaxation of the F center, and that this quenches the luminescence in some manner. If this were the mechanism for the concentration quenching of luminescence, one would expect that the efficiency of luminescence would depend upon the amount of time in which the two centers were in resonance. Thus, excitation with light absorbed on the low-energy side of the F band would lead to luminescence of a greater efficiency than would excitation of higher energy.[15] This model would imply that the excitation spectrum and the absorption spectrum would not agree for all wavelengths. Since the experiment does not confirm this fact, we must infer that energy transfer does not occur between nearby F centers during the relaxation process. It should also be noted that the measurements of the lifetime of the excited state of the F center by Swank and Brown[16] indicate that the quenching process does not compete with the radiative process as a means of providing a relaxation mechanism from the equilibrium excited state.

IV. DATA ON RANDOMLY ORIENTED M CENTERS IN KCl

M centers were introduced into sample 78D by optically bleaching the crystal at room temperature (RT) with 5800Å light in the Cary 14R spectrophotometer for 45 min per side; the resulting crystal is designated sample 79D. The absorption at LNT for the F, R_1, R_2, M, and N_1 bands were 0.503, 0.019, 0.011, 0.188, and 0.000 o.d., respectively. By choosing the constant k in the correction formula to obtain the same peak height in the F-band region for the excitation spectrum as for the absorption spectrum, the two excitation spectra agree well on the long-wavelength side of the F band; but on the short-wavelength side the excitation spectrum becomes increasingly stronger, relative to the absorption, as lower wavelengths are approached (being 60% larger than the absorption at 490 mμ). This means that the η_i are not the same for the F-center and the M-center transitions in the F-band region. In particular, the M_3 and M_3' transitions on the high-energy side of the F band[5] may luminesce more efficiently than the M_2 and M_2' and the F-center transitions.

For excitation into the M band around 800 mμ, only two straight lines between the quarter-maximum positions were needed to fit the excitation and absorption data well in a Gaussian plot. Thus, the M-band absorption and excitation spectra fit double-Gaussian curves very well within the quarter-maximum positions. And further, the efficiency for luminescence of the M center is independent of the wavelength over this region studied.

For given color centers, the luminescence L_k polarized along direction k is[17]

$$L_k=\sum_{i,j,q} I_i m_{jq} n_{jq} \eta_{lq} \cos^2\theta_{ij} \cos^2\theta_{lk},$$

where I_i is the intensity of the incident light polarized in direction i, m_{jq} is the absorption cross section of type-q dipoles aligned along direction j, n_{jq} is the number of type-q dipoles aligned along direction j, θ_{ij} and θ_{lk} are the angles between direction i and j, and between l and k, respectively, and η_{lq} is the efficiency for luminescence of dipoles aligned along direction l, corresponding to a center which absorbs light by type-q dipoles oriented along direction l. Assuming that η_{lq} is independent of l and q, $L_{\max}$ and $L_{\min}$ can be found by varying the direction k, the polarization of luminescence P can then be found by

$$P=(L_{\max}-L_{\min})/(L_{\max}+L_{\min}).$$

For M-band excitation, the q sum is over only the M_1

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[13] J. D. Konitzer and J. J. Markham, J. Chem. Phys. 32, 843 (1960).

[14] W. D. Compton and M. N. Kabler, International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965, Abstract 32 (unpublished).

[15] W. B. Fowler (private communication).

[16] R. K. Swank and F. C. Brown, Phys. Rev. Letters 8, 10 (1962).

[17] J. L. Boettler, Ph.D. thesis, University of Illinois, 1966 (unpublished).

Table I. Polarization of M-center luminescence (in %): comparison between observation (Obs.) and theory (Th.).

Sample	79D		151B		57D	
Temperature	RT		LNT		LNT	
	Obs.	Th.	Obs.	Th.	Obs.	Th.
Emission angle (deg)	90	90	15	0	90	90
Band region excited	F	F	M	M	M	M
Orientation of polarizer						
Vertical [001]	13.8	20	30	33	29	33
Diagonal [011]	6.7	9	62	67	20	20
Horizontal [010]	1.1	0	28	33	2	0

transition, and directions l and j are the same. For F-band excitation, neglecting the F-center luminescence (assuming $\eta_{lq}=0$ for F centers when M centers are present), the q sum is over the M_2 and M_2' transitions; but the luminescence comes from the M_1 transition[1]; so l and j are not the same.

The polarization of luminescence was measured at LNT and RT at several angles. The experimental and theoretical results are given in Table I. The values upon M-band excitation agree well with the van Doorn–Haven model, and with previous measurements.[4,6–8] The values of polarization of luminescence upon F-band excitation are somewhat lower than expected.

The absolute efficiency of luminescence has been determined for the F center,[12,14,18] but not for the M center. Although our apparatus was not adequate to measure the latter directly, it was determined relative to the F-center luminescence. Since the electronic amplification and the intensity of the exciting light could drift slowly with time, each luminescence signal was compared with the luminescence from a neodymium-glass sample. The intensity of luminescence from the neodymium-glass sample was compared with that of F centers at 4.7×10^{16} F centers/cm^3 in KCl sample 121D at LNT, upon F-band excitation; M centers were then formed in the same crystal, obtaining an M-band absorption to sample thickness ratio of 0.23 o.d./mm at LNT. The intensity of luminescence upon M-band excitation in that crystal at LNT was then compared with the intensity of luminescence from the neodymium-glass sample under the same conditions as before. Correcting the results for the angular distribution of radiation for the M centers, for the polarization of the M-center luminescence, for the incident light intensity, for absorption, and for detector response,[17] the ratio of the relative efficiencies for luminescence of the F and M centers in sample 131D was

$$\eta_M/\eta_F = 1.00\mp0.15.$$

Since the F-center concentration of 4.7×10^{16}/cm^3 results in a luminescence efficiency of 85%,[12] the M-center luminescent efficiency should also be 85% in this sample. In all samples, the ratio of the two efficiencies was near 1.0.

V. EXPERIMENTS ON FULLY ORIENTED M CENTERS IN KCl

Starting with a KCl crystal colored by the van Doorn technique, cleaved to 1.09 mm and pulse-annealed like sample 78D, M centers were formed by optically bleaching this crystal at ice temperature (IT) for 40 min/side with yellow-green light.[19] These M centers were then reoriented by optically radiating the crystal at dry ice temperature (DIT: −78°C) for 90 min/side with $[0\bar{1}1]$-polarized green light.[20] The latter radiation treatment was continued for 3 min/side at LNT also, and the resulting crystal was designated sample 113D. The peak absorptions at LNT for light polarized along the $[0\bar{1}1]$ ([011]) direction were: 0.473 (0.721), 0.028 (0.019), and 0.683 (0.036) o.d. for the F-, R_1,- and M-band regions, respectively.

The excitation spectra for this sample were taken using the chopper in position 2 of Fig. 2, replacing the aluminum blade with an infrared polariod, and using an HN32 polaroid oriented in the [011] direction in the excitation beam. The use of a polaroid for the chopper guarantees that a signal will result only if the luminescence is polarized. Thus, the signal arising from the luminescence of centers other than M centers (in particular, F centers) would be minimized. Further, with the orienting process used above, the M_2' transition[5] would not absorb any light when the incident light propagates in the [100] direction. So the excitation spectrum obtained upon excitation into the F-band region is characteristic of the M_2 transition.

The slit widths used here were wider than on previous experiments, and the time constants were longer, to compensate for the weaker signals obtained. Since light of wavelength less than 530 mμ appreciably reoriented the M centers, most measurements were limited to the range between 530 and 620 mμ.

Gaussian plots of the absorption and corrected excitation spectra in the F-band region are shown in Fig. 5. The excitation spectrum should be compared to the three absorption spectra shown: (*1*) *Absorption spectrum measured with light polarized in the* $[0\bar{1}1]$ *direction.* Since the reorienting light used to form this state of the crystal rotated all M centers having M_2 or M_2' transition dipoles along this direction, the only centers remaining to absorb this polarization of light are the F centers. Thus this absorption spectrum is characteristic of F centers. (*2*) *Absorption spectrum measured with light polarized in the [011] direction.* The M_2' dipole transi-

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[18] C. Z. van Doorn, Philips Res. Rept. 13, 296 (1958).

[19] Light from a 200-W mercury lamp was filtered by a copper sulfate solution and by three Corning filters (9788, 4600, and 2424).

[20] Light from a 200-W mercury lamp was filtered by a copper sulfate solution, by three Corning filters (9788, 4600, and 3385), and by an HN32 plastic polaroid oriented along the $[0\bar{1}1]$ axis of the crystal.

TABLE II. Fractional-maximum positions of the spectra for sample 113D (in mμ).

	Symbol in Fig. 5	Red half-maximum wavelength	Peak	Violet half-maximum wavelength
Curve 1	◇	564.5	540.8	514.5
Curve 2	□	565.0	544.5	519.8
Curve 3	○	565.8	546.7	528.0
Excitation	△	566.7	546.2	526.0

tions are all aligned along the [100] direction, and thus can not absorb light traveling in this direction. But the M_2 dipoles are all aligned along the [011] direction, and thus absorb this polarization of light along with the F centers. Thus this absorption measures both the F and M_2 absorptions. *(3) The dichroic absorption spectrum obtained by subtracting spectrum (1) from spectrum (2)*. The absorption due to F centers is presumably the same in spectra (1) and (2), since F-center absorption is isotropic. By subtracting (1) from (2), only the M_2 absorption should remain. Thus, this absorption spectrum is characteristic of the M_2 transition.[5]

The excitation spectrum and the three absorption spectra all are double-Gaussian in shape above 530 mμ, even though absorption spectrum (2) is a superposition of several absorption bands. Below 530 mμ, the spectra curve outward from the straight line drawn to fit the data near the peak, possibly due to the presence of an M_3 transition[5] in this region. Although all four spectra nearly agree in the half-maximum position on the low-energy side, the excitation spectrum agrees best with curve (3) in slope and position. The peak positions of the excitation spectrum are only 0.5 mμ to the violet of curve (3). The half-maximum points on the high-energy side are spread out even more, making it easier to distinguish between the spectra. The excitation spectrum half-maximum here is shifted by only 2.0 mμ to the violet from curve (3), taking the half-maximum positions from the straight line rather than the rounded curve to avoid any complications with the M_3 transition. The values of the peak and half-maximum positions are given in Table II.

Thus the excitation spectrum follows curve (3) much better than the other two, although the agreement is not as good as obtained in most F-center data. Here the half-widths of the excitation spectrum and the dichroic absorption spectrum differ by 3 mμ. The broadening of the excitation spectrum here is due to experimental factors, such as the longer time constants used. The experiment was repeated on several other samples with the same results.

As a check on the assumption that η_F was effectively zero in this experiment, the excitation spectrum was also measured with the exciting light polarized in the [0$\bar{1}$1] direction. The signal obtained was at most 1% of the signal obtained with the excitation light polarized in the [011] direction. Thus the F-center luminescence was effectively eliminated. This means that the luminescence upon exciting the crystal with F-band light polarized in the [0$\bar{1}$1] direction is unpolarized, in agreement with the work of Delbecq.[6] (For comparison, when a mechanical chopper was used instead of the polaroid, this signal was about 50% of the signal obtained with the excitation light polarized in the [011] direction.) In some crystals, where a small amount of R centers was present, the polarization of the luminescence with excitation in the F-band region with light polarized in the [0$\bar{1}$1] direction was negative. This indicates that there are R-center transitions in the F-band region,[7,21] and that the luminescence from these R centers is polarized horizontally rather than vertically out the sides of the crystal. The signal was not strong enough to determine their peak positions nor half-widths, nor to determine how many such bands exist in the F-band region.

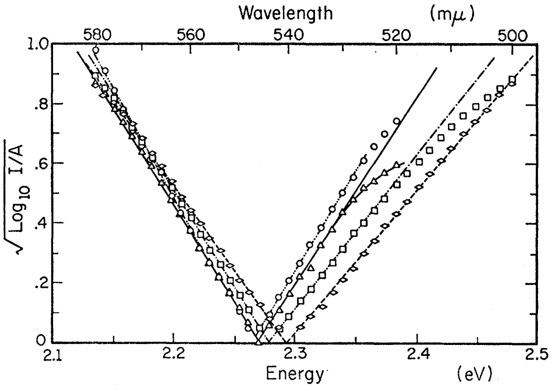

FIG. 5. Gaussian plots of the absorption and excitation spectra of the F band region in sample 113D.

Symbol	Meaning
◇	Curve (1): absorption spectrum measured with light polarized in the [0$\bar{1}$1] direction.
□	Curve (2): absorption spectrum measured with light polarized in the [011] direction.
○	Curve (3): dichroic absorption spectrum obtained by subtracting curve (1) from curve (2).
△	Corrected excitation spectrum, taken with light polarized in the [011] direction.
A	Height of the spectrum at energy E divided by the peak height.

In the HES theory, the excitation spectrum should follow the absorption of the M_2 transition. That is quite true here; the excitation and the dichroic absorption spectra (which are mainly due to the M_2 transition) agree reasonably well above 530 mμ. The efficiency for luminescence of the M_2 transition can be considered constant throughout the band, though the agreement between the absorption and excitation spectra is not as great as it was in the F-center data. Here the agreement is $\mp$15% inside the quarter-maximum point on the low-energy side, and 11% inside the half-maximum points on both sides, using the straight line of the Gaussian

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[21] R. H. Silsbee, Phys. Rev. **138**, A180 (1965).

plots rather than the curved lines for determining these efficiencies.

In the ET theory, the excitation spectrum should follow the total absorption curve (2). Further, η_F should be nonzero even for the experimental setup used here, since the F center should absorb light of any polarization equally well, transfer its energy to the M center, which in turn emits polarized light; this polarized emission should be detected by the present apparatus. Neither of these expectations was verified.

Accepting the HES theory, it is worth inquiring whether one can explain the shape of the excitation spectrum below 530 mμ. The shape of the excitation spectrum changes rapidly near the half-maximum point on the high-energy side, where the efficiency for reorientation of the M centers starts to rise. This change in shape and in reorientation efficiency may be due to the small amounts of the M_3 and M_3' transitions absorbing there.[5] Earlier experiments showed an excitation spectrum peak around 485 mμ (uncorrected for absorption and lamp spectrum), which was not apparent in the absorption spectrum. This is consistent with an absorption corresponding to the M_3 transition hidden under the high-energy side of the F band.

VI. DATA ON NaF

Blum[22] has reported that NaF can be prepared with only M centers present. If this is indeed the case, this material would be particularly useful for studying transitions to the higher excited states without the complication of the overlapping F band. An attempt was made to verify this suggestion.

After x raying a NaF crystal at RT in the dark, the excitation spectrum at LNT of the M band was accurately double-Gaussian between 476 and 514 mμ, and followed the absorption spectrum accurately. Beyond 514 mμ, the spectrum angled over abruptly in the Gaussian plot, indicating the presence of another band. The polarization of luminescence upon M-band excitation agreed well with the van Doorn–Haven model of the M center, for randomly oriented M centers.

After IT bleaching of the above NaF sample with unfiltered Hg light, the polarization of the luminescence indicated that the M centers had been reoriented by the excitation with unpolarized F-band light.

After RT bleaching of the same NaF sample with unfiltered Hg light, other bands appeared both in the absorption and the excitation spectra: One band strongly broadened the red side of the M band; others appeared at 740 and 860 mμ. The polarization of luminescence found with M-band excitation could not be interpreted on a simple model. Though no detailed emission experiments were made, it is estimated that the emission peak of the 740-mμ band (determined by using Corning filters) was around 920 mμ.

After the NaF crystal in the above state was annealed at 70°C in the dark for 17 min, the 740-mμ band disappeared; but no other large changes were observed.

Considering the above NaF data, it is apparent that the techniques used here to develop M centers in KCl cannot be carried over without change to NaF to give only M centers. A complete conversion of F centers into M centers with no other color centers developing, if such a conversion could be obtained, would produce an excellent system in which to study the M_2 transition without any interference from the F center. Further experiments of this type are now being planned.

VII. SUMMARY AND CONCLUSIONS

Excitation spectra were measured for F centers and for two transitions of M centers in KCl. In all three cases, the excitation spectra were double-Gaussian in shape and followed the absorption spectrum closely.

The efficiency of luminescence for F centers at concentrations between 0.4×10^{17} and 3×10^{17} centers/cm^3 with no F-aggregate centers present was independent of the energy of the exciting light used, within 5% inside the quarter-maximum points and within 2% inside the half-maximum points, even though concentration varied the efficiency for luminescence by nearly a factor of 2. This suggests that energy transfer does not occur between nearby F centers during the relaxation of the F center to its equilibrium excited state.

With randomly oriented M centers present, the same results were obtained on the M band, although the excitation spectrum in the F-band region showed an increasing efficiency for luminescence toward the violet tail of the F band, below 530 mμ. This was interpreted to mean that excitation of the M_3 and/or M_3' transitions[5] induced luminescence more efficiently than the superposition of the luminescence of F centers and the excitation of M_2 and M_2' transitions. The efficiency of luminescence of M centers upon M-band excitation was measured relative to the efficiency of luminescence of F centers (with no F-aggregate centers present) at low concentrations, upon F-band excitation; they were found to be equal, within an experimental uncertainty of 15%.

With M centers present and oriented, special techniques were used in the excitation spectra to prevent any unpolarized component of the luminescence from being detected. With these techniques, the excitation spectrum of M centers upon M-band excitation agreed well with the absorption spectrum and with the data on randomly oriented M centers; thus the spectra were double-Gaussian in shape and the efficiency for luminescence was independent of the wavelength of the exciting light in the M-band region.

Using the same techniques in the F-band region, the excitation spectrum was double-Gaussian in shape. It followed the dichroic absorption spectrum corresponding to the absorption due to the M_2 transitions much

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[22] H. Blum, Phys. Rev. **128**, 627 (1962).

better than it followed the total absorption for the incident light polarized in either direction (parallel or perpendicular to that used in the excitation spectrum). These data support the hypothesis that transitions to HES[1,5,4] of the M center occur in the wavelength region of the F band, and that energy is not being transferred from F centers to nearby M centers (ET).[7]

The efficiency of luminescence of the M_2 transition was independent of the wavelength of the exciting light within 15% inside the quarter-maximum point on the red side, and within 11% inside the half-maximum points of the absorption curve on both sides.

The same excitation spectra showed that an M_3 transition was present and luminesced more efficiently than the M_2 transition. Excitation below 530 mμ resulted in more efficient reorientation of the M centers than excitation above 530 mμ. It is not clear whether this is due to the M_3 and M_3' transitions affecting reorientation more than the M_2 and M_2' transitions, or to the higher energy of the exciting light.

Optical bleaching, absorption-, and excitation-spectrum experiments showed that other bands are present in NaF which have not been previously reported. There is a band on the red tail of the M band; and bands appear at 740 and 860 mμ, all of which luminesce. The 740-mμ band can be annealed out at 70°C. It is apparent that the techniques used to develop M centers in KCl cannot be carried over, unaltered, to NaF to obtain a complete conversion of F centers into M centers, with no other color centers developing.

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Optical Phonons of Yttrium Aluminum Garnet

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The dielectric properties and optical phonons of yttrium aluminum garnet (YAG) have been studied by measurements of the infrared (IR) reflection spectra and the Raman effect. A factor group analysis of the YAG space group shows that there are 18 T_{1u} IR-active modes, and 3 A_{1g}, 8 E_g, and 14 T_{2g} Raman-active modes. The IR data have been interpreted by a Kramers-Kronig transform to yield values of the complex dielectric constant and frequencies of the longitudinal and transverse long-wavelength T_{1u} modes. 15 of the 17 predicted T_{1u} optic modes have been observed. All the A_{1g} and E_g modes have been identified, but at least 3 of the 14 T_{2g} modes are missing from the observed Raman spectra.

I. INTRODUCTION

THE crystal structure of garnets was found by Menzer[1] to belong to the space group $Ia3d(O_h^{10})$, a body-centered cubic Bravais lattice and a member of the cubic O_h crystal class. The unit cell consists of eight molecules of $P_3Q_2(RO_4)_3$. Cations P, Q, and R have 8, 6, and 4 nearest oxygen neighbors, and are situated respectively at the 24(c), 16(a), and 24(d) sites whose positions are defined in terms of the cubic cell edge a; the positions of the 96(h) sites of the oxygen anions depend upon three more parameters x, y, z.[2] Interest in the garnets has been concentrated mainly on a few compositions for which the (a) and (d) sites have the same ions. In particular, the diamagnet yttrium aluminum garnet (YAG), $Y_3Al_2(AlO_4)_3$, and its derivatives with a rare-earth element substituting for yttrium, and the ferrimagnet yttrium iron garnet (YIG) with similar derivatives. The former system is ideal for the study of rare-earth ions in both dilute and concentrated form and is used as a host material for the neodymium 1.06-μm laser. YIG is an important ferrite, and becomes an almost unique system for the study of indirect rare-earth–iron interactions when a rare-earth is substituted for the yttrium. Wood and

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[1] G. Menzer, Z. Krist. **69**, 300 (1928).

[2] This nomenclature and the position of the (a), (d), (c), and (h) sites can be found in the *International Tables for X-Ray Crystallography* (Kynoch Press, Birmingham, England, 1964), Vol. I.