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Optical Absorption of *M* Centers in Potassium Chloride Crystals*

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The optical absorption of *M* centers in potassium chloride crystals has been studied by observing the anisotropy induced in the crystals after bleaching with polarized light. It is found that the *M* center has absorption bands hidden under the *F* band in addition to an absorption in the 800-mμ region. The observed anisotropy near the *F* band is the result of the presence of other absorption bands in the *F*-band region. The optical absorptions of *R* and *N* centers have also been studied. The change in the location and half-width of the *F* band during bleaching can be accounted for by the presence of secondary centers.

INTRODUCTION

SINCE Ueta[1] demonstrated the anisotropic nature of the *M* center by partial bleaching with polarized light, several experiments have been reported in recent years which deal with symmetry properties of *M* centers. Van Doorn and Haven[2] have shown that at liquid nitrogen temperature, a reorientation of *M* centers is induced by irradiation with polarized *F*-band light, and that both the *F* and *M* bands show anisotropy. The same type of anisotropy in the *F* and *M* bands has been observed at room temperature after partial bleaching of the *M* band with polarized light.[3,4] It is also known that absorption of polarized light by the *F* band produces polarized luminescence from *M* centers, if both *F* and *M* centers are present in the crystal.[4–6]

Two alternative interpretations have been proposed in order to account for the close relationship between *F* and *M* centers: (1) The anisotropy in the *F*-band region is the result of transitions to higher excited states of the *M* center which overlap the *F*-band absorption.[4,5] (2) Energy transfer processes can occur between *F* and *M* centers, and the observed anisotropy in the *F* band is ascribable to an interaction of *F* centers with neighboring *M* centers.[3–6]

The present work was undertaken to determine the optical absorption of *M* centers, especially in the *F*-band region, by irradiating the crystal with polarized light and observing the anisotropy induced in the optical absorption spectrum. (Since the completion of this paper, three papers bearing on the subject matter related to the optical absorptions and their anisotropic properties of the *M*, *R*, and *N* centers have been published by others.[7–9] The results of this paper are in substantial agreement with theirs.)

EXPERIMENTAL PROCEDURES

Single crystals of pure KCl were obtained from the Harshaw Chemical Company. Color centers were produced in the crystals by heating in potassium vapor or by γ-ray irradiation from a 4000-curie Co^{60} source. The initial concentration of *F* centers in the crystals ranged from 1×10^{16} to 4×10^{17} cm^{-3}, while the thickness of the crystals varied from 0.3 to 10 mm.

Polarized light was obtained by using an Ahrens prism which was mounted on the Dewar flask used to hold the crystal. Absorption spectra were taken at liquid nitrogen temperature on a Cary model 14*R* spectrophotometer in the wavelength range from 400 to 1700 mμ using polarized light. The light from the monochromator passed through the polarizing prism and then through the crystal to the detector. An AH-6 lamp or a filament lamp with appropriate filters was used as a light source in the bleaching experiments. To eliminate any temporary change in the optical absorption spectrum after the irradiation with light, all spectra were taken after allowing the crystals to stand in the dark for 5 min.

Experiments were performed on both additively colored KCl and γ-irradiated KCl, but no essential differences were found.

EXPERIMENTAL RESULTS

Experiments with Unpolarized Light

A crystal containing only *F* centers was irradiated at room temperature with unpolarized *F*-band light. The *F* band decreased continuously and was accompanied by a slight increase of the absorption in the short wavelength tail of the *F* band. The *M* band grew during the early stages of the exposure and decreased after reaching a maximum. *R* and *N* bands grew continuously until they attained an equilibrium value. During the exposure, the *F* band broadened and the absorption maximum shifted first to the red and then

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‡ Based on a thesis submitted to the Graduate School of Kyoto University in partial fulfillment of the requirements for the degree of Doctor of Sciences.

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

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

[3] H. Kanzaki, Phys. Rev. **110**, 1063 (1958).

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

[5] C. Z. van Doorn and Y. Haven, Philips Research Repts. **11**, 479 (1956); C. Z. van Doorn, Philips Research Repts. **12**, 309 (1957).

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

[7] H. Pick, Z. Physik **159**, 69 (1960).

[8] T. Tomiki, J. Phys. Soc. Japan **15**, 488 (1960).

[9] K. Fukuda, A. Okuda, and Y. Uchida, J. Phys. Soc. Japan **15**, 538 (1960).

to the violet while *M* and *R* bands grew, respectively.[10] The maximum ratio of *M* center concentration to *F* center concentration was largest in crystals which contained the highest initial concentration of *F* centers. For initial concentrations less than about 10^{17} cm^{-3}, the crystals showed a prominent *N* band and an absorption band at about 1460 *m*μ. Curve 2 of Fig. 2(a) shows the absorption spectrum of a crystal at the stage where the *M* band reached its maximum.

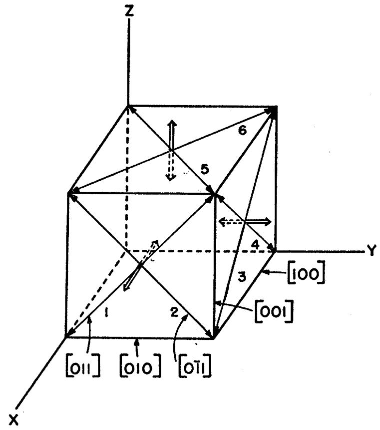
The crystal which is represented by curve 2 of Fig. 2(a) was brought to liquid nitrogen temperature and irradiated with unpolarized *F*-band light. As shown by curve 3 of Fig. 2(a), the 1460-mμ band disappeared and another absorption band was formed at about 1380 mμ. Slight changes also occurred in other regions of the absorption spectrum. On warming the crystal to room temperature, the 1460-mμ band was reformed at the expense of the 1380-mμ band.

Experiments with Polarized Light

1. *Irradiation with* $[011]$ *Light*[11]

Curve 3 of Fig. 2(a) shows the absorption spectrum taken with either unpolarized, $[011]$, or $[0\bar{1}1]$ light before irradiation with polarized light. After irradiation at liquid nitrogen temperature with $[0\bar{1}1]$ *F* light[12] the absorption became anisotropic and the intensities of the spectra taken with $[011]$ and $[0\bar{1}1]$ light were not equal as shown by curves 4_1 and 4_2 of Fig. 2(a). If the $[0\bar{1}1]$ absorption is subtracted from the $[011]$ absorption, a difference curve is obtained which is the anisotropic absorption[13] produced in the crystal by the irradiation; this subtraction eliminates all other absorptions which do not show anisotropy under these

FIG. 1. The possible orientations of the optical dipole moments related to the M_1 band (single arrow) and to the M_2' band (double arrow).



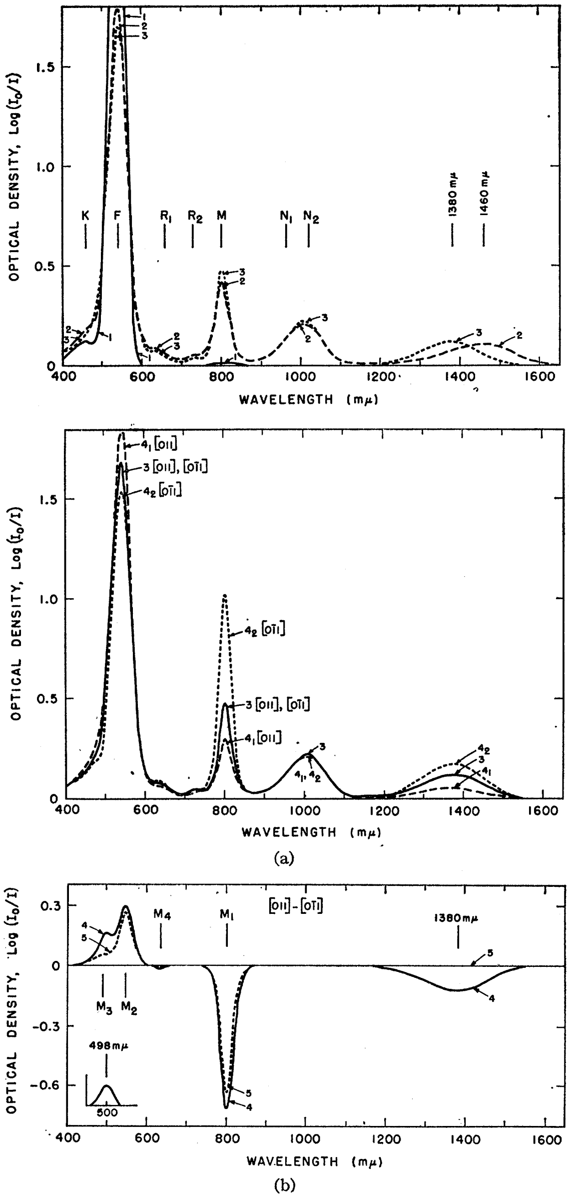


FIG. 2. The absorption spectra of an additively colored KCl crystal 10 mm thick. (a) Curve (1), after quenching from 400°C ($N_F{}^0=1.38\times10^{16}$ cm^{-3}); (2), after 5-min irradiation with unpolarized *F* light at room temperature; (3), plus 1-hr irradiation with unpolarized *F* light at liquid nitrogen temperature measured with either unpolarized, $[011]$, or $[0\bar{1}1]$ light; and then after irradiation with $[0\bar{1}1]$ *F* light at liquid nitrogen temperature for 2 hr. as measured with $[011]$ light (4_1) and $[0\bar{1}1]$ light (4_2). (b) Curve (4), the anisotropic absorption obtained by subtraction of curve (4_2) from curve (4_1); and (5), the remaining anisotropic absorption after warming to room temperature for 10 min.

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[10] J. D. Konitzer and J. J. Markham, Phys. Rev. **107**, 685 (1957).

[11] The term "$[0\bar{1}1]$ light" will be used to indicate light with electric vector parallel to $[0\bar{1}1]$ and with propagation vector parallel to $[100]$, and the term "$[100]'$ light" will be used to indicate light with electric vector parallel to $[100]$ and with propagation vector parallel to $[010]$. These directions are related to the crystal axes (Fig. 1).

[12] The term "*F* light" will be used to indicate light from an AH-6 lamp in conjunction with a 547-mμ interference filter and Corning filters 3486 and 9788, and the term "*M* light" will be used to indicate light from a filament lamp in conjunction with Corning filters 2-2600 and 3384 which have a maximum transmission at about 820 mμ.

[13] This constitutes a definition of anisotropic absorption as used in this paper.

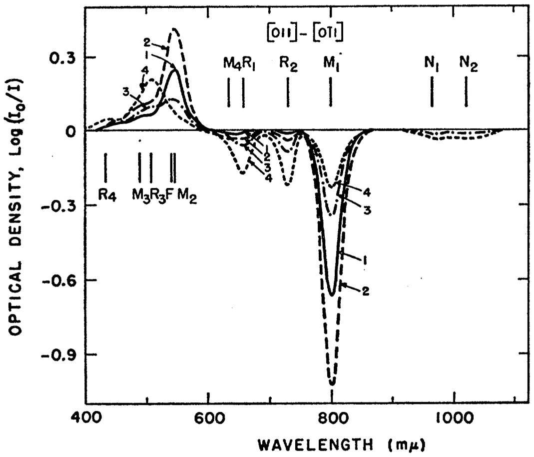


FIG. 3. The anisotropic absorption obtained by subtraction of the $[0\bar{1}1]$ absorption from the $[011]$ absorption after irradiation with $[0\bar{1}1]$ F light at room temperature (1) for 5 min; (2) plus 5 min; (3) plus 30 min; and (4) plus 2 hr. (Additively colored crystal 0.8 mm thick, $N_F{}^0=1.74\times10^{17}$ cm^{-3}).

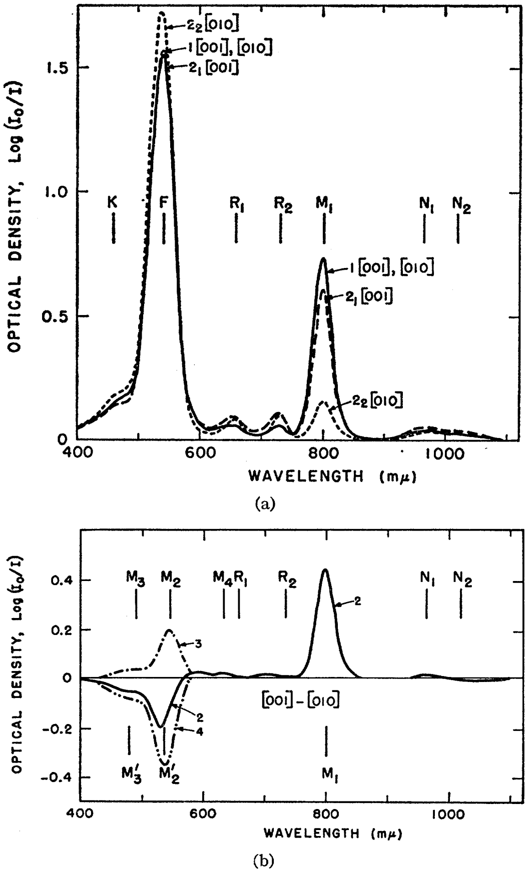
conditions. Curve 4 of Fig. 2(b) shows the absorption obtained by subtraction of curve 4_2 of Fig. 2(a) from curve 4_1. Curve 5 shows the anisotropic absorption obtained after the crystal was warmed to room temperature for 10 min in order to eliminate anisotropy in the 1380-mμ region. During this annealing process, a small anisotropy at 498 mμ also disappeared. The anisotropic absorption at 498 mμ was obtained by subtraction of curve 5 (normalized) of Fig. 2(b) from curve 4 and is shown in the same figure. As shown by curve 5, in addition to the anisotropies observed at 546 mμ and 801 mμ, small anisotropic absorptions at 634 mμ and in the short-wavelength tail of the 546-mμ band were also observed. The signs of the main anisotropic absorption bands were opposite to each other. It should be noted that if the initial concentration of F centers exceeded 10^{17} cm^{-3}, irradiation with $[0\bar{1}1]$ F light at liquid nitrogen temperature induced only small anisotropies.

A crystal containing F and M centers was irradiated with $[0\bar{1}1]$ M light at 0°C. After the irradiation the absorption spectra were taken with $[011]$ and $[0\bar{1}1]$ light. The anisotropic absorption obtained by subtraction of the $[0\bar{1}1]$ absorption from the $[011]$ absorption was identical with that shown by curve 5 of Fig. 2(b) except for sign reversal.

An anisotropic growth of M, R_1, R_2, N_1, and N_2 bands was also studied. A crystal containing only F centers was irradiated with $[0\bar{1}1]$ F light at room temperature, and the absorption spectra were taken with $[011]$ and $[0\bar{1}1]$ light in successive stages of the irradiation. Figure 3 shows the absorption obtained by subtraction of the $[0\bar{1}1]$ absorption from the $[011]$ absorption. At the beginning of the irradiation, the anisotropy in the 801-mμ band increased together with that in the 546-mμ band. Upon further irradiation, both the absorption and anisotropy at 801 mμ decreased and the anisotropy in the R_1, R_2, N_1, and N_2 bands increased. At the same time, the anisotropy at 546 mμ shifted to 508 mμ.

2. *Irradiation with [010] Light*

A crystal containing F and M centers whose absorption spectrum was similar to that shown by curve 3 of Fig. 2(a), was irradiated with $[010]$ F light at liquid nitrogen temperature. After the irradiation the absorption spectra were taken with $[010]$ and $[001]$ light. The anisotropic absorption obtained by subtraction of the $[001]$ absorption from the $[010]$ absorption was similar to that shown by curve 2 of Fig. 4(b), which was obtained after irradiation with $[010]$ M light at 0°C. However, the intensity of the anisotropic spectrum was much weaker in the irradiation with F light. For equal irradiation, the anisotropy induced by irradiation with $[010]$ F light was a factor of 10 less than that induced by irradiation with $[0\bar{1}1]$ F light.



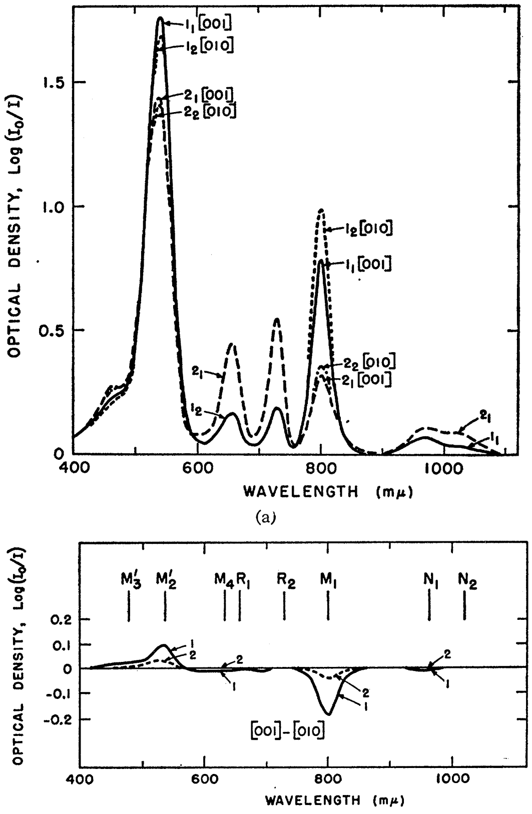
(a)

(b)

FIG. 4. The absorption spectra of an additivley colored KCl crystal 0.6 mm thick ($N_F{}^0=1.74\times10^{17}$ cm^{-3}). (a) After 13-min irradiation with F light at 0°C as measured with (1) either unpolarized, $[001]$ or $[010]$ light; and then after irradiation with $[010]$ M light at 0°C for 40 min as measured with $[001]$ light (2_1) and $[010]$ light (2_2). (b) Curve (2), the anisotropic absorption obtained by subtraction of curve (2_2) from curve (2_1); calculated anisotropic absorptions of the M_2 and M_3 bands (3) and of the M_2' and M_3' bands (4).

A crystal containing *F* and *M* centers was irradiated with [010] *M* light at 0°C. Curve 1 of Fig. 4(a) shows the absorption spectrum taken with either unpolarized, [011] or [010] light before the irradiation. After the irradiation, the absorption became anisotropic and the intensities of the spectra taken with [001] and [010] light were not equal as shown by curves 2_1 and 2_2 of Fig. 4(a). Curve 2 of Fig. 4(b) shows the anisotropic absorption obtained by subtraction of curve 2_2 from curve 2_1. The rate of the development of the anisotropy was about the same as that induced by the irradiation with $[0\bar{1}1]$ *M* light at 0°C, but the location of the band maximum in the *F*-band region was not identical with the latter.

The anisotropic growth of *M*, R_1, R_2, N_1, and N_2 bands was also studied. A crystal containing only *F* centers was irradiated with [010] *F* light at room temperature, and the absorption spectra were taken with [001] and [010] light at two stages in the irradiation. The results are shown in Fig. 5(a). At the beginning of the irradiation, the *F* band decreased and the *M* band at 801 mμ increased anisotropically as shown by curves 1_1 and 1_2. As shown by curves 2_1 and 2_2 upon further irradiation both the absorption and anisotropy in the *F* and *M* band regions decreased and the absorptions in the R_1, R_2, N_1, and N_2 band regions increased but showed no anisotropy. Curves 1 and 2 of Fig. 5(b) show the anisotropic absorptions obtained by subtraction of curve 1_2 of Fig. 5(a) from curve 1_1, and of curve 2_2 from curve 2_1, respectively. The anisotropic spectra obtained were similar to those shown in Fig. 4(b); however, the intensity of the anisotropic absorption was much smaller.



(a)

(b)

FIG. 5. The absorption spectra of an additively colored KCl crystal 0.4 mm thick ($N_F{}^0=3.36\times10^{17}$ cm^{-3}). (a) After irradiation with [010] *F* light at room temperature for 6 min as measured with [001] light (1_1) and [010] light (1_2); plus 30 min more irradiation as measured with [001] light (2_1) and [010] light (2_2). (b) The anisotropic absorptions obtained by subtraction of (1) curve (1_2) from curve (1_1), and (2) curve (2_2) from curve (2_1).

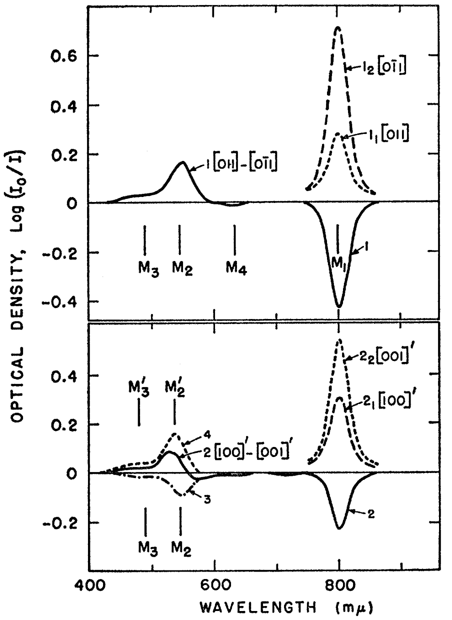


FIG. 6. The absorption spectra of an additively colored KCl crystal 6.6 mm thick ($N_F{}^0=1.90\times10^{16}$ cm^{-3}) after irradiation with $[0\bar{1}1]$ *F* light at liquid nitrogen temperature for 3 hr 10 min as measured with [011] light (1_1), $[0\bar{1}1]$ light (1_2), [100]′ light (2_1), and [001]′ light (2_2); anisotropic absorptions obtained by subtraction of (1) curve (1_2) from curve (1_1), and (2) curve (2_2) from (2_1); and anisotropic absorptions of (3) the M_2 and M_3 bands and of (4) the $M_2{}'$ and $M_3{}'$ bands.

3. *[011], $[0\bar{1}1]$, [100]′, and [001]′ Spectra.*

A more detailed study of the anisotropy was made by taking the [011], $[0\bar{1}1]$, [100]′, and [001]′ spectra. In order to measure the absorption spectra from the lateral direction of the crystal, a thick crystal was used. The crystal containing *F* and *M* centers was irradiated with $[0\bar{1}1]$ *F* light at liquid nitrogen temperature. Curves 1 and 2 of Fig. 6 show the anisotropic absorption obtained by subtraction of the $[0\bar{1}1]$ absorption from the [011] absorption, and of the [001]′ absorption from the [100]′ absorption, respectively. Individual spectra in the 800-mμ region taken with [011], $[0\bar{1}1]$, [100]′, and [001]′ light are also shown in the figures. The anisotropic spectrum represented by curve 1 is identical with that shown by curve 5 of Fig. 2(b), and that represented by curve 2 is similar to curve 2 of Fig. 4(b).

TABLE I. Characteristics of *R*- and *N*-center absorptions.

Absorption band	R_1	R_2	R_3	R_4	N_1	N_2
Orientation	⟨111⟩	⟨111⟩	⟨111⟩	⟨111⟩	⟨110⟩	⟨111⟩
Band maximum (mμ)	658	730	508	434	964	1020
Half-width (ev)	0.10	0.06	0.23	···	···	···
Band height	$0.80h_{R_2}$	h_{R_2}	$0.78h_{R_2}$	$0.17h_{R_2}$	···	$0.15h_{R_2}$

A short and incomplete study was also made of the anisotropic absorptions associated with *R*, *N*, and other unknown centers in the crystal. In the following experiments, crystals containing the maximum amount of *R* and *N* centers were used; in these crystals the height of the *M* band at 801 mμ was about half of that of the R_2 band. Figure 7 shows the anisotropic absorption obtained by subtraction of the [0$\bar{1}$1] absorption from the [011] absorption after irradiation with [0$\bar{1}$1] light of wavelength 701 mμ.[14] The R_1, R_2, N_1, and N_2 bands and the *F* band region showed anisotropy. On the other hand, [010] light of wavelength 701 mμ induced no anisotropy in the R_1 and R_2 bands. Figure 8 shows the anisotropic absorption obtained by subtraction of the [0$\bar{1}$1] absorption from the [011] absorption after irradiation with [0$\bar{1}$1] light of wavelength 1000 mμ.[15] The R_1, R_2, N_1, and N_2 bands and the *F*-band region showed anisotropy. On the other hand, [010] light of wavelength 1000 mμ induced anisotropy in the N_1 band and in the *F*-band region as shown in Fig. 9. The anisotropic spectrum in the *F*-band region was not obtained because of the high intensity of the *F* band. [010] light of wavelength 701 mμ induced anisotropy similar to that shown in Fig. 9, but the amount of the anisotropy was much smaller. In these experiments the *M* band region at 800 mμ always showed anisotropy but the location of the band maximum shifted to the long-wavelength side of the *M* band. The origin of this band and the other anisotropic bands at about 600 and 700 mμ shown in Fig. 9 is not known. A summary of the results obtained for *R* and *N* centers is given in Table I, where the R_3 and R_4 bands indicate the anisotropic absorption bands in the *F*-band region.

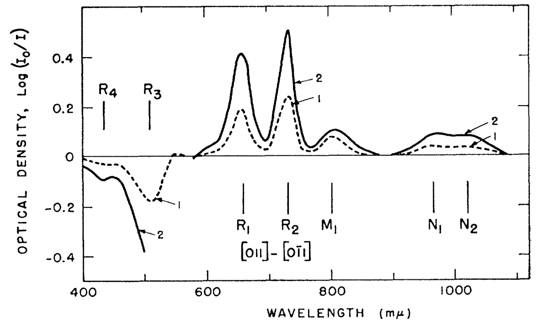


FIG. 7. The anisotropic absorptions obtained by subtraction of the [0$\bar{1}$1] absorption from the [011] absorption after irradiation at room temperature with [0$\bar{1}$1] light of wavelength 701 mμ (1) for 70 min (γ-irradiated crystal 0.5 mm thick, $N_F^0=1.86\times10^{17}$ cm^{-3}); and (2) for 2 hr (additively colored crystal 2.3 mm thick, $N_F^0=1.62\times10^{17}$ cm^{-3}).

DISCUSSION

Two simple experiments are sufficient to determine whether the optical dipoles of anisotropic centers are oriented parallel to ⟨100⟩, ⟨110⟩, or ⟨111⟩ directions[16]: (1) If anisotropies are produced in the [011] and [0$\bar{1}$1] spectra after bleaching with [0$\bar{1}$1] light the optical dipoles are not aligned along ⟨100⟩ but may be along ⟨111⟩ or ⟨110⟩. (2) If anisotropies are produced in the [001] and [010] spectra after bleaching with [010] light, the optical dipoles are not aligned along ⟨111⟩, but may be along ⟨100⟩ or ⟨110⟩. Consequently, only centers with dipole moments oriented parallel to ⟨110⟩ directions show anisotropy after irradiation with either [0$\bar{1}$1] or [010] light.

Since the *M* band at 801 mμ becomes anisotropic after irradiation with either [0$\bar{1}$1] or [010] *M* light, it is concluded that the optical dipole responsible for the *M* band is oriented along ⟨110⟩ directions of the crystal. It is very improbable that other absorption bands overlap the *M* band since the location and half-width of the band observed in the anisotropic spectrum were identical with those of the original *M* band irrespective of the direction of the polarized light used for the irradiation. This conclusion is consistent with the results obtained in experiments on the polarization of luminescence from *M* centers.[4–6]

If a second *M* band is assumed to overlap the *F*

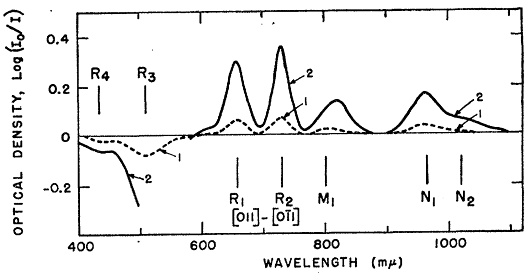


FIG. 8. The anisotropic absorptions obtained by subtraction of the [0$\bar{1}$1] absorption from the [011] absorption after irradiation at room temperature with [0$\bar{1}$1] light of wavelength 1000 mμ (1) for 10 min (γ-irradiated crystal 0.4 mm thick, $N_F^0=1.86\times10^{17}$ cm^{-3}); and (2) for 2 hr (additively colored crystal 2.3 mm thick, $N_F^0=1.62\times10^{17}$ cm^{-3}).

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[14] Light from a filament lamp in conjunction with a 701-mμ interference filter and Corning filter 3384.

[15] Light from a filament lamp in conjunction with Corning filters 2-2540 and 3384 which have a maximum transmission at about 1000 mμ.

[16] W. D. Compton and C. C. Klick, Phys. Rev. **110**, 349 (1958).

TABLE II. Characteristics of M-center absorptions.

Absorption band	M_1	M_2	M_3	M_4	M_2'	M_3'
Orientation	$\langle 110\rangle$	$\langle 110\rangle$	$\langle 110\rangle$	$\langle 110\rangle$	$\langle 100\rangle$	$\langle 100\rangle$
Band maximum (mμ)	801	546	490	634	538	480
Half-width (ev)	0.07	0.16	...	...	0.19	...
Oscillator strength	f	$1.0f$	...	...	$1.0f$	...
Band height	h_{M_1}	$0.41h_{M_1}$	$0.08h_{M_1}$	$0.025h_{M_1}$	$0.73h_{M_1}$	$0.17h_{M_1}$

band, the F-band region should become anisotropic when the M band at 801 mμ shows anisotropy, and a quantitative relation should exist between the amount of anisotropy in the F- and the M-band regions. Further, the location and half-width of the bands observed in the anisotropic absorption should be independent of the amount of the anisotropy induced, of the method used to induce the anisotropy, and of the concentration of F and M centers. According to the experimental results, the anisotropies induced by irradiation with $[0\bar{1}1]$ F light and with $[0\bar{1}1]$ M light were identical as determined by the conditions mentioned above. The second M band is located at 546 mμ and the ratio of the height of the second M band to that of the M band at 801 mμ was 0.41. The concentration of F and M centers used in the experiments varied by more than a factor of 20. Therefore, it is concluded that the anisotropy induced in the F-band region is a result of the presence of a second M band overlapping the F band. The second M band will be called the M_2 band while the M band at 801 mμ will be called the M_1 band.

The experiments show that the optical dipole moments responsible for the M_1 band and the M_2 band are at right angles to each other and oriented along the face diagonals of the crystal lattice. The six distinguishable orientations of the dipole moments responsible for the M_1 band are illustrated in Fig. 1. Using this model of the M center, one can compute the absorption coefficients of the M_1 and M_2 bands in terms of the concentration of M centers oriented in the six directions. If M centers are equally distributed among the six orientations, the absorption coefficients for unpolarized light are expressed as $A_0^{(1)}=2\alpha N_0$ and $A_0^{(2)}=2\beta N_0$, for the M_1 and M_2 bands, respectively, where α and β are positive constants, $A^{(1)}$ and $A^{(2)}$ signify the absorption coefficients for the M_1 and M_2 bands, respectively, and N_0 is the concentration of M centers in any of the six orientations. Absorption coefficients measured with $[011]$ and $[0\bar{1}1]$ light after irradiation with $[0\bar{1}1]$ F or M light can be computed in the same way and the anisotropic absorption is represented by the difference of the two absorption coefficients, that is,

$$\Delta A_{M_1}=A_{[011]}{}^{(1)}-A_{[0\bar{1}1]}{}^{(1)}=\alpha(N_1-N_2),$$

and

$$\Delta A_{M_2}=A_{[011]}{}^{(2)}-A_{[0\bar{1}1]}{}^{(2)}=-\beta(N_1-N_2), \qquad (1)$$

since $N_1\neq N_2\neq N_3=N_4=N_5=N_6$, where N_i is the concentration of M centers whose optical dipole moment responsible for the M_1 band is oriented in the direction (1) in Fig. 1, and $A_{[011]}{}^{(1)}$ denotes the absorption coefficient of the M_1 band measured with $[011]$ light. In Eqs. (1), N_1 is smaller than N_2 for the irradiation with $[0\bar{1}1]$ F light and N_1 is larger than N_2 for the irradiation with $[0\bar{1}1]$ M light. In either case, the anisotropic absorption in the F band region (M_2 band) is expected to have an opposite sign to that of the M_1 band, and the ratio of the peak height, $\Delta A_{M_2}/\Delta A_{M_1}$, will be equal to a constant, β/α. The constancy of the ratio was confirmed experimentally. The weak anisotropic absorptions in the short-wavelength tail of the M_2 band and at 634 mμ have not been reported previously,[17] but from the present work they are believed to be related to M centers, since the anisotropies were always induced at definite wavelengths when the M_1 and M_2 bands became anisotropic, and the relative heights of the absorptions to the M_1 and M_2 bands were constant. In order to make identification easier these bands will be called M_3 and M_4 bands, respectively. Table II shows the locations of band maxima, half-widths, relative oscillator strengths, and relative band heights of the M_1, M_2, M_3, and M_4 bands.

Absorption coefficients measured with $[001]$ and $[010]$ light after irradiation with $[010]$ F or M light can be expressed in a similar manner to that described previously, and the absorption coefficients obtained in the anisotropic absorption will take the form:

$$\Delta A_{M_1}=A_{[001]}{}^{(1)}-A_{[010]}{}^{(1)}=\alpha(N_3-N_1),$$

and

$$\Delta A_{M_2}=A_{[001]}{}^{(2)}-A_{[010]}{}^{(2)}=\beta(N_3-N_1), \qquad (2)$$

since $N_1=N_2=N_5=N_6\neq N_3=N_4$. It is expected that

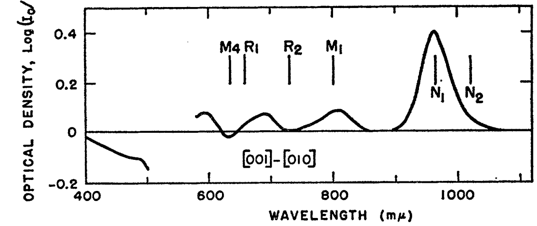

FIG. 9. The anisotropic absorptions obtained by subtraction of the $[010]$ absorption from the $[001]$ absorption after irradiation at room temperature for 2 hr with $[010]$ light of wavelength 1000 mμ (additively colored crystal 2.3 mm thick, $N_F{}^0=1.62\times10^{17}$ cm^{-3}).

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[17] Concurrent to this work, F. Lüty also observed similar bands, which were shown on a slide at the Color Center Symposium, Corvallis, Oregon, 1959.

N_1 will be smaller than N_3 for both irradiation with F light or with M light, that the anisotropic absorption in both M_1 and M_2 band regions will have the same sign, and that the ratio of the peak height, $\Delta A_{M_2}/\Delta A_{M_1}$, will be equal to that obtained by the irradiation with $[0\bar{1}1]$ light, i.e., β/α. According to the experimental results the sign of the anisotropy is opposite in the M_1 and M_2 band regions and the location of the band maximum of the anisotropic absorption in the F band region is displaced to shorter wavelengths by about 10 $m\mu$ from that of the M_2 band. Furthermore, the rate of the development of the anisotropy upon irradiation with $[010]$ F light is much smaller than that with $[0\bar{1}1]$ F light, whereas the rates observed in bleaching with $[010]$ M light and with $[0\bar{1}1]$ M light are almost the same. In order to account for the peculiarity observed in the irradiation with $[010]$ F light, it is assumed that there exists another dipole oriented perpendicular to the aforementioned two kinds of dipoles responsible for the M_1 and M_2 bands, and that the dipoles are oriented parallel to cubic axes of the crystal, i.e., $\langle 100\rangle$ directions. In addition, the optical absorption associated with the dipoles lies in the F-band region of the spectrum. The absorption band which is assumed to arise from the dipoles oriented in the $\langle 100\rangle$ directions will be called the M_2' band. The possible orientations of the dipoles are denoted by double arrows in Fig. 1.

First, consider the anisotropy induced by irradiation with $[010]$ M light. M light does not affect the dipoles oriented along $\langle 100\rangle$ directions since the excitation energy is assumed to correspond to the light in the F-band region. Therefore, Eqs. (2) will hold for the anisotropy induced in the M_1 and M_2 bands, but in addition, the anisotropy due to the M_2' band must also be considered. The absorption coefficient of the M_2' band in the anisotropic absorption will be expressed as

$$\Delta A_{M'_2}=A_{[001]}{}^{(2')}-A_{[010]}{}^{(2')}=-2\gamma(N_3-N_1), \quad (3)$$

where γ is a positive constant for the M_2' band. It should be noted that the sign of the anisotropy in the M_2' band is opposite to those of the M_1 and M_2 bands. Since it is assumed that both M_2 and M_2' bands are located in the F band region, the apparent ansiotropic absorption in that region will be the sum of the anisotropies of the two bands. Equations (2) show that the ratio, $\Delta A_{M_2}/\Delta A_{M_1}$, is equal to β/α, which is the same as that obtained by irradiation with $[0\bar{1}1]$ light, and that the anisotropic absorption of the M_2 band has the same sign as that of the M_1 band. It is therefore possible to calculate the anisotropic absorption of the M_2 band for a known amount of anisotropy in the M_1 band. The anisotropic absorption of the M_2 band thus estimated is given by curve 3 of Fig. 4(b). The anisotropy of the M_2' band will be the numerical sum of this calculated absorption and the observed anisotropic absorption in the F band region, [curve 4 of Fig. 4(b)]. As seen in the curve, the M_2' band is accompanied by an absorption on its short-wavelength tail. The absorption will be called M_3' band in analogy to the M_3 band. Table II shows the locations of band maxima, half-widths, relative oscillator strengths, and relative band heights of the M_2' and M_3' bands.

The presence of dipoles oriented along $\langle 100\rangle$ directions may be used to explain the slow development of the anisotropy during irradiation with $[010]$ F light. If a crystal containing M centers is irradiated with $[010]$ F light, the centers in positions 1, 2, 5, and 6 of Fig. 1 are excited since the dipoles along face diagonals interact with $[010]$ F light. On the other hand, the centers in positions 3 and 4 are also excited since the dipoles parallel to cubic axes will also interact with $[010]$ F light. These two processes will compete with each other and retard the development of the anisotropy. If the crystal is irradiated with $[010]$ M light, the development of the anisotropy will be much faster since in this case the centers in positions 3 and 4 are not excited. If $[0\bar{1}1]$ F or M light is used to induce anisotropy, the dipoles oriented along $\langle 100\rangle$ directions do not contribute to the anisotropic absorption obtained by subtraction of the $[0\bar{1}1]$ absorption from the $[011]$ absorption since they are cancelled by the subtraction. Therefore, Eqs. (1) preserve their validity for the measurements with $[011]$ and $[0\bar{1}1]$ light after irradiation with $[0\bar{1}1]$ F or M light. If absorption spectra are taken with $[100]'$ and $[001]'$ light after the irradiation, however, the dipoles oriented along $\langle 100\rangle$ directions will also show anisotropy. The absorption coefficients in the anisotropic absorption measured with $[110]'$ and $[001]'$ light will be expressed as

$$\Delta A_{M_1}=A_{[100]'}{}^{(1)}-A_{[001]'}{}^{(1)}=\tfrac{1}{2}\alpha[2N_3-(N_1+N_2)],$$

$$\Delta A_{M_2}=A_{[100]'}{}^{(2)}-A_{[001]'}{}^{(2)}=\tfrac{1}{2}\beta[2N_3-(N_1+N_2)],$$

and

$$\Delta A_{M'_2}=A_{[100]'}{}^{(2')}-A_{[001]'}{}^{(2')}=-\gamma[2N_3-(N_1+N_2)]. \quad (4)$$

These equations show that the ratios, $\Delta A_{M_2}/\Delta A_{M_1}$ and $\Delta A_{M'_2}/\Delta A_{M_1}$, are the same as those obtained in Eqs. (2) and (3). Accordingly, the anisotropic absorption thus obtained is expected to be similar to that measured with $[001]$ and $[010]$ light after irradiation with $[010]$ F or M light. The experimental results are consistent with this expectation as shown in Fig. 6, where curves 3 and 4 correspond to those in Fig. 4(b). The locations of band maxima, half-widths, relative oscillator strengths, and relative band heights of the M_2' and M_3' bands obtained from Fig. 6 agree with those given in Table II within experimental error.

In summary it is concluded that the M center has absorptions bands in the F band region in addition to the so-called M band at 801 mμ and that the observed anisotropy in the F-band region is ascribable to the M bands hidden under the F band. Although it has been assumed that the M_1, M_2, and M_2' bands arise from three different transitions, the same results would have been obtained if the M_2 and M_2' bands arose from the same transition but have slightly different characteristics when excited with ⟨110⟩ or ⟨100⟩ light because of differences in local crystal fields in these two directions. The characteristics of the M-band absorptions reported here are not inconsistent with the present models of the M center.[5,18] The origins of the M_3, M_3', and M_4 bands are unknown except that these bands are closely connected with the M center, and therefore are probably additional absorptions of the M center.

In the course of the present investigation, it was also observed that the absorption of polarized light by the R and N bands induces anisotropy in the F band region. Therefore, the R and N centers will have an important role in the anisotropy induced in the F band region if these centers are present in the crystal. As shown in Figs. 3 and 5, $[0\bar{1}1]$ F light induces anisotropy in the R_1, R_2, N_1, and N_2 bands whereas [010] F light induces no appreciable anisotropy in these bands except a very small one in the N_1 band. Therefore, it is believed that the centers associated with the R_1, R_2, N_1, and N_2 bands have other absorption bands under the F band and that the dipoles associated with the R_1, R_2, and N_2 bands are oriented along ⟨111⟩ directions and those associated with the N_1 band are oriented along ⟨110⟩ directions of the crystal.[19] The R_1, R_2, N_2, and two absorption bands in the F-band region are closely related to each other and probably arise from a single center, while the N_1 band is not related to any of the above bands. The results shown in Figs. 7–9 are consistent with the above conclusions.

The results of the present investigation suggest that in order to obtain the anisotropic absorption of M centers only, caution must be taken to avoid the anisotropy of other centers such as R and N centers. The change in the location and half-width of the F band during bleaching of F centers[10] is explicable by the overlapping of the M_2 and R_3 bands with the F band. At the beginning of the bleaching of F centers, M centers are formed, and upon further bleaching R centers are formed, accompanied by a decrease in M centers. Since the band maxima of the F, M_2, and R_3 bands are located at 540, 546, and 508 mμ, respectively, the absorption in the F-band region will shift to the long-wavelength side of the initial F band and then to the short-wavelength side in the course of the formation of the M and R centers. There seems to be no direct connection between the K band and M and R centers since the K band appears even in crystals which do not contain M or R centers.[10] However, the presence of M and R bands in the F-band region should be taken into consideration in the study of the K band.

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