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New *F*-Type Color Center in CsBr Crystals Doped with Cl^- Ions

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A new absorption band consisting of two components is found in additively colored CsBr crystals doped with Cl^- ions. It is suggested that the corresponding color center, called F_H, consists of an F center adjacent to a Cl^- ion. Dichroic bleaching properties are described. The luminescence is characterized by a single Gaussian emission band, peaking at 1.5 eV and with a half-width of 0.17 eV. The temperature dependence of the emission is different for the two components of the excitation spectrum.

INTRODUCTION

The aggregation of F centers in alkali halides or the perturbation of F centers by foreign neighboring ions give rise to new color centers, such as M, R, F_A, and Z centers. They are obtained by bleaching of the F band in the appropriate temperature range. The F_A center, which is an F center perturbed by a foreign alkali ion, has been intensively studied by Lüty and co-workers.[1] It gave direct evidence about the influence of reduced symmetry and exchanged cation neighbors on the optical properties of an F center. So far, the only experimental evidence of the influence of exchanged monovalent anion neighbors is given by the shift of the F band in x-rayed KCl-KBr mixed crystals.[2]

We have found new optical absorption bands in additively colored CsBr single crystals containing foreign halogen ions by irradiation in the F band. Experimental evidence is given that indicates that this absorption can be attributed to a new color center, that we call F_H, indicating that the F center is adjacent to a foreign halogen ion. We have not yet investigated similarly treated alkali-halide single crystals having the NaCl structure.

This paper reports the optical absorption, dichroic optical bleaching, and the luminescence due to F_H centers in CsBr single crystals doped with Cl^- ions.

EXPERIMENTAL

The crystals were grown by the Bridgeman-Stockbarger method from Merck "Suprapur" CsBr powder. An undoped crystal was grown to make sure that the F_H band does not appear in that case. An addition of 0.2% CsCl is appropriate to produce a well developed F_H band. The crystals were additively colored in K vapor at 500°C and quenched immediately before mounting in the cryostat. When the concentration of Cl^- ions is too high, additive coloration becomes increasingly difficult.

The orientation of the crystals was performed on an x-ray goniometer with an accuracy of 2°. Absorption spectra were measured with a Cary-15 spectrophotometer. For measurements with polarized light a polaroid foil was used.

Emission spectra were analyzed with a Bausch & Lomb grating monochromator and detected with a Philips-150 CVP photomultiplier. The measured data were corrected for the relative spectral response of the detection system so that the proper emission curve is obtained. For the excitation, a 450-W Xe arc with interference filters centered at 575 and 600 nm was used. The excitation spectra were taken with the same Bausch & Lomb monochromator in the excitation path and the emission measured through an 825-nm interference filter and a Schott-Jena RG8 filter. The relative spectral distribution of the exciting light was determined with a radiation thermocouple. To measure the degree of polarization of the luminescence a polaroid foil was used as a polarizer and a Glan-Thompson prism as an analyzer.

Temperatures between liquid-helium temperature (LHT) and liquid-nitrogen temperature (LNT) were measured with a gold-(cobalt)-versus-normal-silver thermocouple and higher temperatures with a copper-constantan thermocouple.

RESULTS

Optical Absorption

Figure 1 shows the absorption spectrum mesaured at different temperatures, of an additively colored CsBr crystal containing 0.2% CsCl, after irradiation in the F band at 170° K. At the short-wavelength side of the F band a new absorption band appears with two maxima which are well resolved at 15°K. The maximum at 1.94 eV in curve a is due to the residual F band. The new absorption band probably has two components, but so far a proper decomposition into two Gaussian curves was not possible. However, by comparing the spectra in different samples it seems likely that the relative height of the two components remains constant. We concluded that the double absorption band is due to one center and called it the F_H band. As the temperature increases, the maxima shift to longer wavelengths and the half-width increases in a similar way as for the F band.

A similar absorption band is also found in CsBr crystals containing fluorine ions.

Optical Bleaching

The F_H band can be partly bleached at 100°K by irradiation with F_H light. Figure 2 shows the absorption

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[1] A review is given by F. Lüty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968).

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

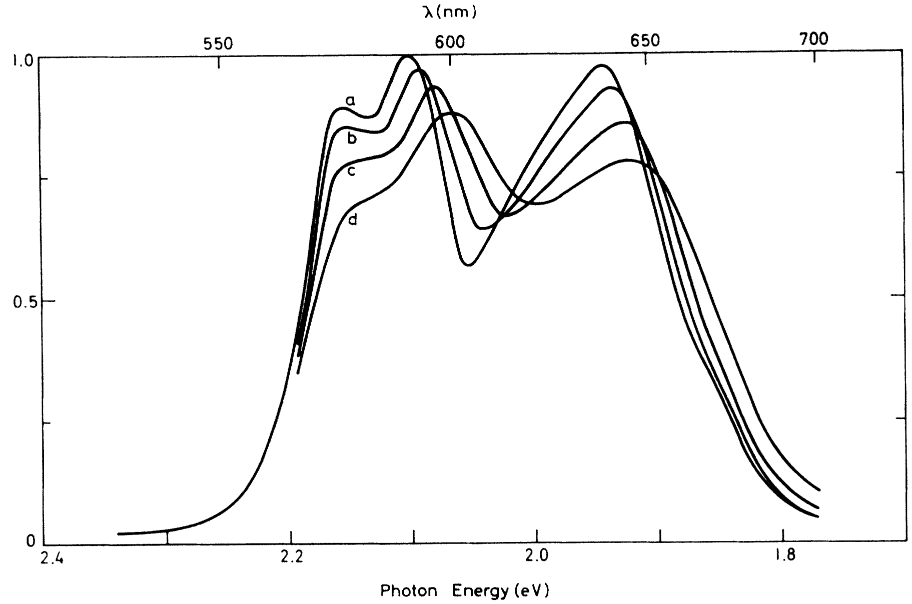

FIG. 1. Absorption spectra of additively colored CsBr: Cl^- single crystals after irradiation with 650-nm light at 170°K: curve a, 15°K; b, 36°K; c, 55°K; d, 79°K.

spectrum at LNT before and after this optical bleaching. The F centers formed by the destruction of the F_H centers can be converted into F' centers with F light at LNT and recovered by irradiation at 800 nm. Irradiation in the F band at 170°K after the $F_H \rightarrow F$ conversion does not restore the F_H band, but M centers are formed. However, a subsequent irradiation in the M band (at 1.04 μ) at this temperature, again creates F_H centers.

The F_H band can also be bleached at 15°K with light in the range 400–550 nm as can be seen in Fig. 3. The initial absorption is completely restored after irradiation with light of 800 nm at 15°K. In this case no ionic movement is possible. The F_H centers are apparently ionized while the electron is captured in a shallow trap from which it can succeedingly be liberated. This trap does not seem to be α centers or F centers as the height of the F band remains unchanged. The background in the F'-band region increases and eventually F_H' centers could be formed.

Oriented crystals were bleached with linearly polarized light incident perpendicular to the (100) plane. F_H-band dichroism can be introduced by irradiation in each of the two components of the F_H band with [010]- or [001]-polarized light (Fig. 4). This is due to a dichroic destruction of the F_H centers since no reorientation could be observed. On the other hand, bleaching with [011] polarized light did not introduce any dichroism, indicating that the F_H centers have their transition dipole parallel to a [100] direction. We have not been able to observe a second transition perpendicular to this one.

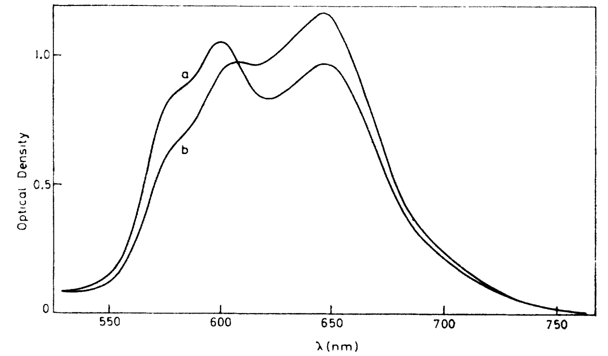

FIG. 2. Absorption spectra at LNT of CsBr:Cl^- containing F_H centers before (curve a) and after (curve b) irradiation in the F_H band at 100°K.

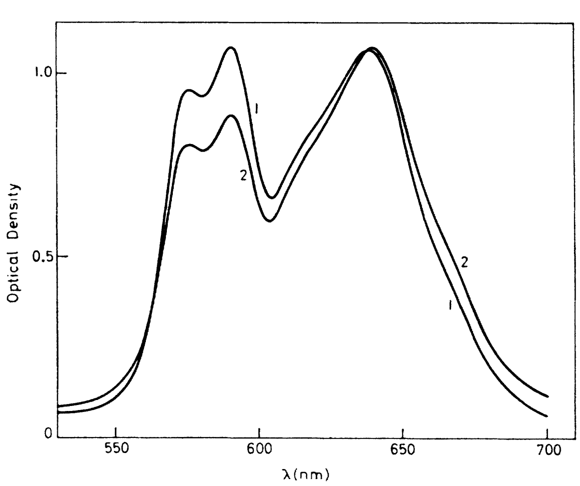

FIG. 3. Absorption spectra at LNT of CsBr:Cl^- containing F_H centers before (curve 1) and after (curve 2) irradiation at 400–550 nm.

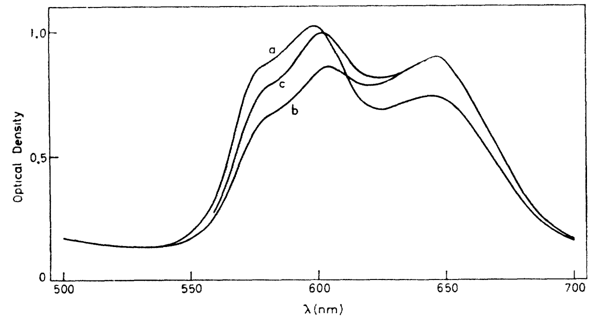

FIG. 4. Curve a, original absorption spectrum at LNT of CsBr: Cl$^-$ containing F_H centers. After bleaching with [001] polarized light the absorption spectrum is measured with [001] polarized light (curve b) and [010] polarized light (curve c).

LUMINESCENCE

Emission Spectrum

Figure 5 shows the spectral distribution of the luminescence at different temperatures due to excitation in the F_H band. The same emission band is found for excitation at 575 and 600 nm. At 15°K it can be described by a symmetrical Gaussian curve peaking at 1.50 eV and with a half-width of 0.17 eV. This can be seen from a plot of $[\ln (I_0/I)]^{1/2}$ as a function of the photon energy as shown in Fig. 6. I_0 is the intensity at the peak of the emission band and I is the intensity at any photon energy. However, there is a small deviation in the long-wavelength tail, but this is only slightly larger than the experimental error at this wavelength. The luminescence decreases rapidly when the temperature is raised. At higher temperatures the shift of the emission band to longer wavelength and the variation of the half-width are small but comparable to what is found for an F center in the same temperature interval.

Excitation Spectrum

The excitation spectrum at 15°K for the emission at 825 nm is shown in Fig. 7. A complex band with three components is found in the F_H-band region. Bleaching of the F_H band by irradiation 400–550 nm also causes a decrease of the luminescence. Excitation with a 900-W Xe arc through a 475-nm interference filter seems to give rise to an emission similar to the F_H emission. The signal is weak, however, since the absorption is also small, so that no detailed study is possible. The luminescence experiments also indicate that the two components at 575 and 590 nm belong to the F_H center. This is apparently not the case for the 615-nm band, but it is too small to take an emission spectrum. Figure 8 shows the excitation spectrum at three different temperatures. At higher temperatures the two main excitation peaks become equal, while the third soon disappears. This is a surprising result. We followed the emission during the warm-up, exciting alternatively at 575 and 590 nm (Fig. 9). The spectral bandwidth of the exciting light was 3 nm. Between 15 and 20°K the temperature changed rapidly, and the results were not reproducible. This was not the case at higher temperatures. One observes that the emission excited at 590 nm increases with temperatures up to the point where it is the same

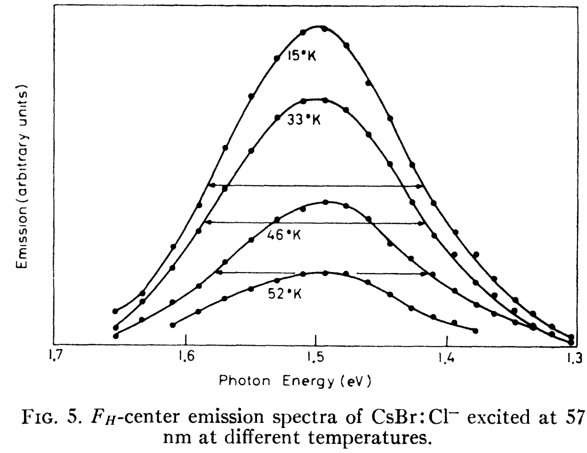

FIG. 5. F_H-center emission spectra of CsBr:Cl$^-$ excited at 575 nm at different temperatures.

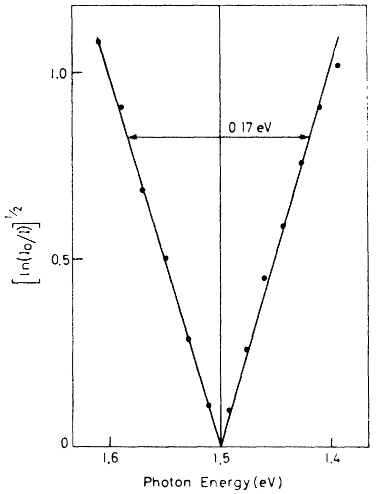

FIG. 6. $[\ln I_0/I]^{1/2}$ versus photon energy for F_H center luminescence in CsBr:Cl$^-$ at 15°K.

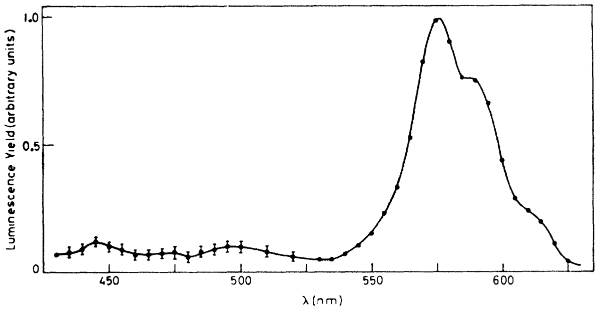

FIG. 7. Excitation spectrum at 15°K for 825-nm luminescence of CsBr$^-$Cl: containing F_H centers. The ordinate is the emitted intensity per photon incident on the crystal.

as the emission excited at 575 nm. Above 30°K the two signals have the same temperature dependence. The points marked by a triangle in Fig. 9 are the peak values of emission spectra some of which are shown in Fig. 5.

The degree of polarization of the emission was measured at 15°K. The linearly polarized exciting light was propagating in the [100] direction and the emission measured in the same direction. Figure 10 shows the excitation spectra for light polarized in the [001] and with the analyzer parallel and perpendicular to this direction. One observes that the emission excited at 575 and 590 nm is not polarized, while the emission excited at 615 nm is completely polarized. This suggests that the 615 nm excitation is not due to F_H absorption.

DISCUSSION AND CONCLUSION

F_H centers can only be created in CsBr crystals containing foreign halogen ions. They are formed in the same conditions in which F aggregate centers are formed. Bleaching experiments confirm that the F center is a part of the aggregate. We suggest that the F_H center consists of an F center adjacent to a foreign halogen ion. The symmetry axis of this center lies in one of the [100] directions. This is confirmed by the bleaching experiments with polarized light.

In the case of F_A centers, irradiation with polarized light causes a reorientation of the centers even at low temperatures. This is possible because the activation energy for the F center to jump around a smaller cation is smaller than the dissociation energy. In the case of the F_H centers in the NaCl structure, alignment of the system should be possible, just as in the case of the M center. In the CsCl structure any jump of the F center to an adjacent position destroys the complex, leaving behind an isolated halogen ion and an F center.

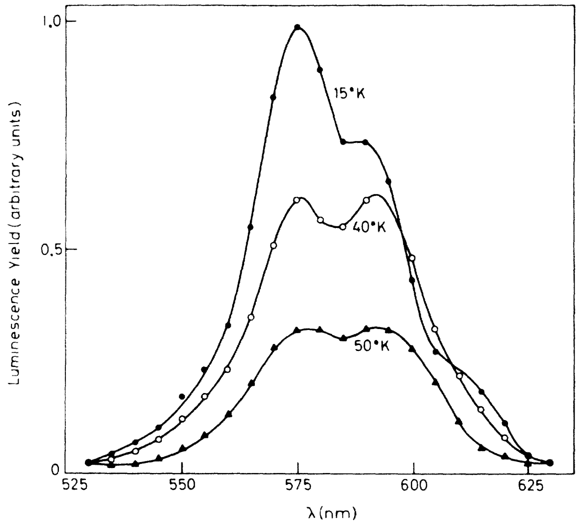

FIG. 8. Excitation spectra of CsBr:Cl$^-$ containing F_H centers at different temperatures.

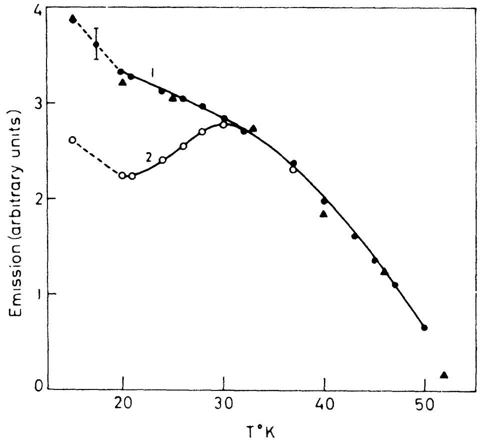

FIG. 9. Temperature dependence of emission excited at 575 (curve 1) and 590 nm (curve 2). The triangles indicate the peak intensities of the emission spectra, some of which are shown in Fig. 5.

So far, there is no evidence that the F_H center has an absorption under the F band as do other aggregate centers. The absorption spectrum at LHT and the excitation curve confirm the existence of two components. They are probably due to spin-orbit splitting of the first excited state as in the case of the F center. The bleaching at 15°K in the short-wavelength region of the spectrum would indicate the existence of one or more higher excited states. The absorption bands were too weak to determine their position. They would correspond to the L bands for the F center.

It is worthwhile to note the difference in luminescence characteristics between the F and the F_H centers: 1. The Stokes shift is about 1 eV in the case of the F center, while it is only about 0.6 eV for the F_H center. 2. The emission spectrum of the F_H center is a symmetrical Gaussian curve compared to the double Gaussian found

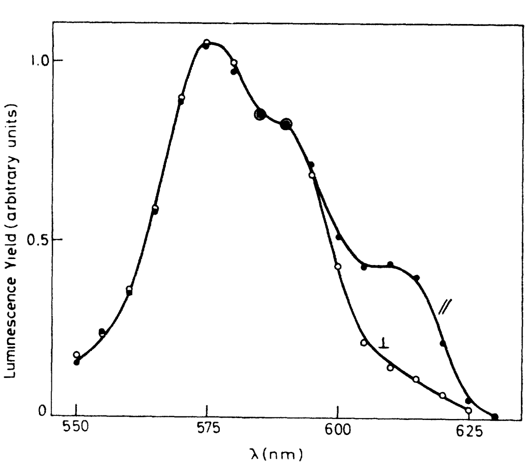

FIG. 10. Excitation spectra with [001] polarized light of CsBr: Cl$^-$ containing F_H centers. The emission intensity in the [001] direction is marked with dots and in the [010] direction with circles.

for the F center. 3. The different temperature dependences of the emission of the two F_H-band components has to be compared with the results of Lynch, Brothers, and Robinson[3] for the F center. However, although these authors do not reveal this property, their excitation spectrum shows more structure then the absorption spectrum. Both were only measured at 13°K. It would be interesting to measure the low-temperature behavior of the emission for the two components of the F band using a narrow spectral bandwidth for excitation.

In the case of the F_H center, the excited state is still split up after lattice relaxation. The temperature behavior of the emission of the 590-nm component at low temperatures seems to indicate that it is thermally activated. The appearence of only one structureless emission band could indicate that the luminescence starts from one single level. Measurements of the radiative lifetime at low temperatures for the two components could perhaps give more information about the luminescence mechanism.

ACKNOWLEDGMENTS

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[3] D. W. Lynch, A. D. Brothers, and D. A. Robinson, Phys. Rev. **139**, A285 (1965).

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Optical Phonons in Sodium Chlorate

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The frequencies of the optical phonons in $NaClO_3$ have been located by measuring the infrared reflectivity and the Raman scattering spectra. By using the Lyddane-Sachs-Teller relationship, a value of 5.6 was found for the static dielectric constant. Dielectric transition strengths were determined from the transverse-longitudinal frequency splitting and found to agree well with prior values obtained by analyses of infrared data. The reflection spectrum, the index of refraction, and the absorption coefficient have been determined throughout the range of the lattice resonances.

INTRODUCTION

WITHIN the past few years, since the application of the laser to the technology of Raman spectroscopy, scattering from several crystals has been studied. In general, the emphasis has been placed on single uniaxial ionic crystals where the complexity of the spectrum was compatible with the development of the theoretical understanding. Considerable emphasis is now being devoted to the more complex crystals, including those of low symmetry with few atoms per unit cell and those of high symmetry with many atoms per unit cell. Sodium chlorate is an excellent representative example of the latter case. It is cubic, belonging to the T^4 space group,[1] and is, therefore, also optically active. There are 4 molecules (20 atoms) per unit cell, resulting in 60 degrees of freedom. The lattice is ionic, consisting of sodium and chlorate ions. Furthermore, the chlorate ions show strong intraionic forces and may therefore be treated as a unit, giving the material molecular-crystal-like features.

Several Raman studies of $NaClO_3$ have been made in the past.[2–5] However, the results of these early investigations were not reliable, since there were "extra" lines in some regions of the spectrum and "missing" lines in other regions. In addition, different frequency values were obtained by each investigator, and there was disagreement as to the assignments of observed lines. These inconsistencies may have resulted from any of several effects. First, $NaClO_3$ is optically active.[6] When laser sources were not available, it was necessary to illuminate a large volume of the crystal to obtain sufficient intensity to make Raman observations. Large crystalline dimensions allowed appreciable angles of optical rotation, and subsequent depolarization errors in the spectra then resulted. Secondly, the point group of sodium chlorate (T) contains A and E irreducible representations, both of which have only diagonal com-

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[2] A. Rousset, J. Laval, and R. Lochet, Compt. Rend. **216**, 886 (1943).

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