Two-photon absorption of color centers in NaF

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Two-photon absorption cross sections of the N_1 and F_3^+ centers in NaF have been determined by means of the luminescence excited by the two-photon absorption. The measured polarization dependence of the process led us to attribute the excitation to the $A_g \rightarrow A_g$ transition in the N_1 center and to the $A \rightarrow E$ transition in the F_3^+ center.

I. INTRODUCTION

Two-photon spectroscopy is widely used today to investigate the optical properties of matter.[1-3] The results of this research are often complementary to those obtained by ordinary one-photon spectroscopy. Two-photon absorption can be measured directly or deduced from the emission that ensues after the absorption takes place. In this latter way one really measures two-photon excitation. This technique does not yield as much information as the direct two-photon absorption spectroscopy, where one measures the absorption at different wavelengths, while the sample is simultaneously irradiated by a second light source. The indirect method is however much more sensitive and indeed it was the first to be used to measure two-photon effects of impurities in solids.[4]

In the case of color centers, where the number of absorbing centers seldom exceed 10^{17} cm^{-3}, the technique of measuring the emission following the two-photon absorption seemed the most appropriate and easy to apply. Indeed the effects to be measured are at least four orders of magnitude smaller that those observed in band-to-band two-photon absorption in solids with 10^{21} electrons cm^{-3}. The shortcomings of the method are the possible loss of information on other processes (nonradiative transitions or photochemical reactions) that may take place together with the radiative emission. The main results of the present work are the first evaluations of two-photon absorption cross sections in color centers in sodium fluoride.

II. EXPERIMENTAL

Crystals of NaF were chosen for this investigation because color centers in this material have absorption bands in the green region of the spectrum (i.e., at twice the laser energy) while their emissions fall in the yellow-red region. Therefore the interfering effects of the absorption band and of the laser light are kept to a minimum.

NaF single crystals, obtained from Harshaw Chemical Co., from the Naval Research Laboratory or home grown where exposed to rays from a ^{60}Co source (~10^5 R/h) for several hours at room temperature. The irradiated samples contained a large amount of F and F-aggregate centers.[5,6] With thermo-optical bleaching at 100 °C with uv light, the F centers were further converted into aggregate centers. After this treatment, the average concentrations of the M, N_1, and F_3^+ centers were $N_M = 4 \times 10^{16}$ cm^{-3}, $N_{N_1} = 2 \times 10^{15}$ cm^{-3}, $N_{F_3^+} = 3 \times 10^{15}$ cm^{-3}. Remember that the N_1 center is an aggregate of four F center forming a parallelogram of vacancies on the $\{111\}$ plane and that the F_3^+ center is the ionized F_3 center which consists of three F centers forming an equilateral triangle on the $\{111\}$ plane.

One of the crystals was doped with NaOH in order to provide oxygen traps for the electrons. In this way the ionized F_3^+ centers are stabilized and after the thermo-optical treatment they outnumber all other centers in the crystal.[7]

The block diagram of the experimental apparatus is shown in Fig. 1. The sample were excited at liquid-nitrogen temperature with a Q-switched YAlG:Nd laser (Holobeam 255 Q) that delivers approximately 4×10^{15} photons/pulse (repetition rate 10^4 sec^{-1}). The unpolarized beam was focused to a spot of 10^{-2} cm^2. Some measurements have been performed with linearly polarized or right-hand circularly polarized photons obtained with a Brewster Stack Polarizer placed in the cavity plus a $\frac{1}{4}\lambda$ delay. Filters (Corning 2-64) were used to remove from the exciting beam the light of the arc lamp. The luminescence was dispersed by a double prism Leiss monochromator and detected by a cooled photomultiplier. The signal was measured by a single photon counter whose gate was triggered by the laser pulse by means of a fast photodiode. An auxiliary optical dispersive system, shown in the upper part of Fig. 1, was used for measuring the absorption of the sample along the

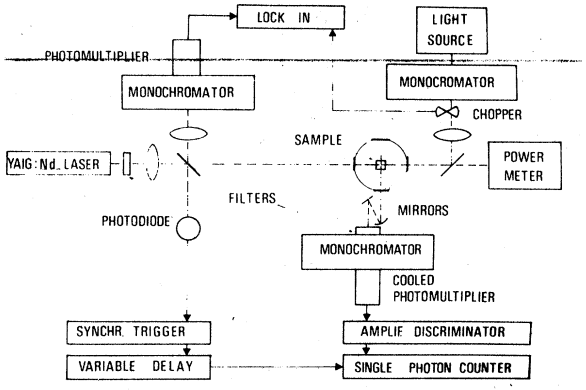

FIG. 1. Experimental apparatus.

same path traversed by the laser beam.

The emission data have been corrected for the spectral sensitivity of the apparatus and the absolute calibration was performed with a blackbody standard source and with the known F-center emission from a weakly colored KCl sample.

III. RESULTS

A typical absorption spectrum of a sample of NaF with aggregate centers used in this experiment is shown in Fig. 2. The number of photons emitted during the laser excitation in a sample containing mainly N_1 centers (3×10^{15} cm^{-3}) are plotted in Fig. 3 as a function of wavelength. The scale of the ordinates indicates the number of photons emitted per laser pulse, over the entire solid angle of 4π, in a bandwidth of 50 Å. Analogous results for a sample containing also F_3^+ centers (2.5×10^{15} cm^{-3}) are shown in Fig. 4. Beside the bands visible in Figs. 3 and 4 the emission continues in the infrared with a broad band that we have attributed to laser stimulated "hot fluorescence."[8]

The luminescence bands at 580 and 660 nm are emission following the two-photon excitation of the

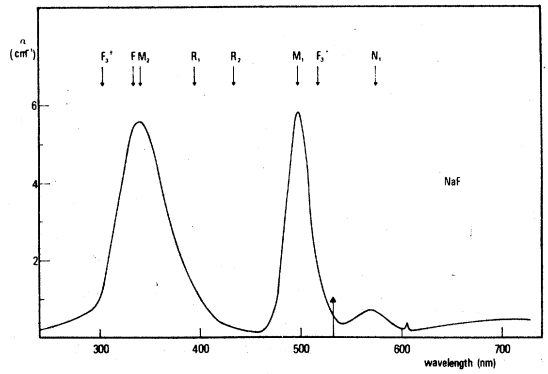

FIG. 2. Absorption spectrum of a colored NaF crystal containing aggregate centers.

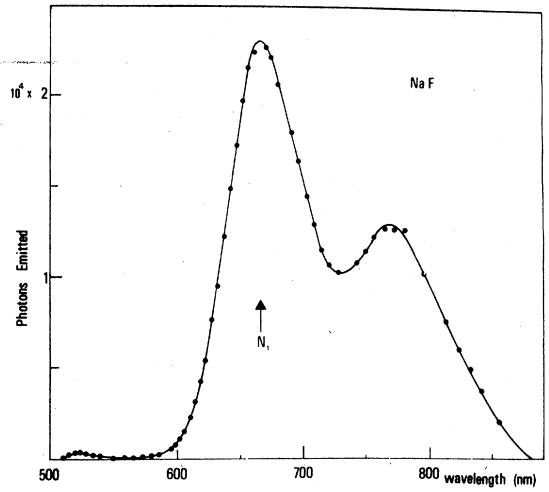

FIG. 3. Two-photon stimulated emission of NaF crystal containing mainly N_1 centers. The scale of the ordinates shows the number of photons emitted per laser pulse, over the entire solid angle of 4π, in a bandwidth of 50 Å.

F_3^+ and N_1 centers, respectively. Their intensities increase with the square of the incident power as shown in Figs. 5 and 6. The emission at 580 nm coincides in position and halfwidth with the known

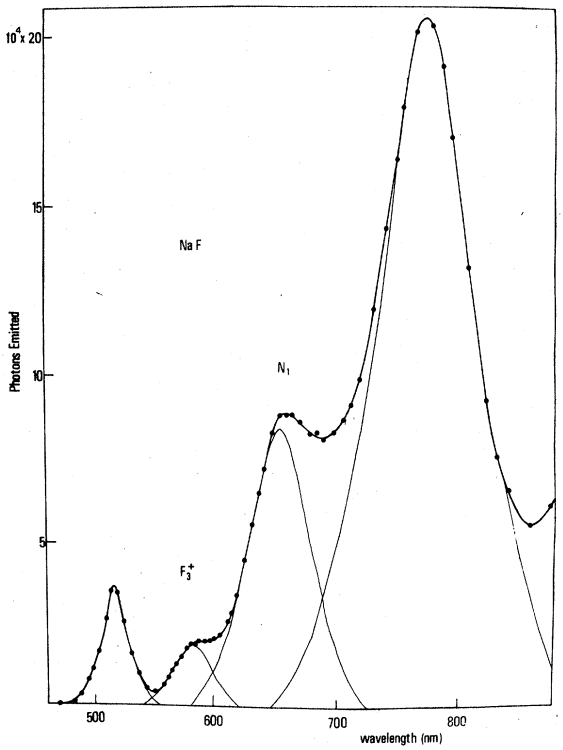

FIG. 4. Two-photon stimulated emission of NaF crystal containing F_3^+ and N_1 centers. The scale of the ordinates shows the number of photons emitted per laser pulse, over the entire solid angle of 4π, in a bandwidth of 50 Å.

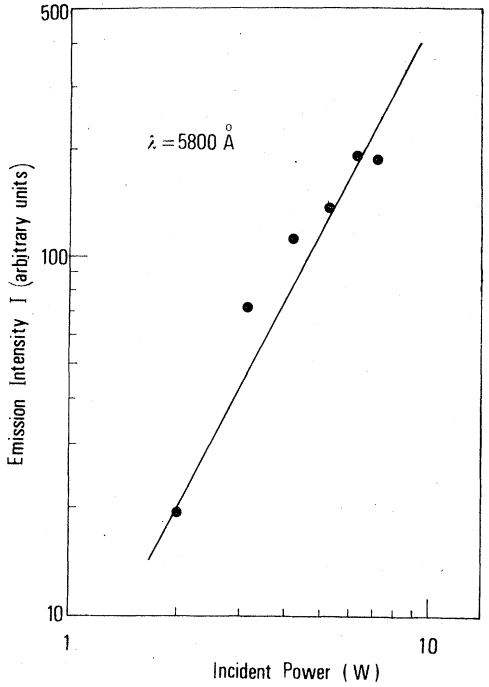

FIG. 5. Emission intensity of the F_3^+ centers as a function of the incident power. The slope of the full line shows the theoretical (quadratic) dependence of the emission intensity on the incident power for a two-photon process [see text, Eqs. (2) and (3)].

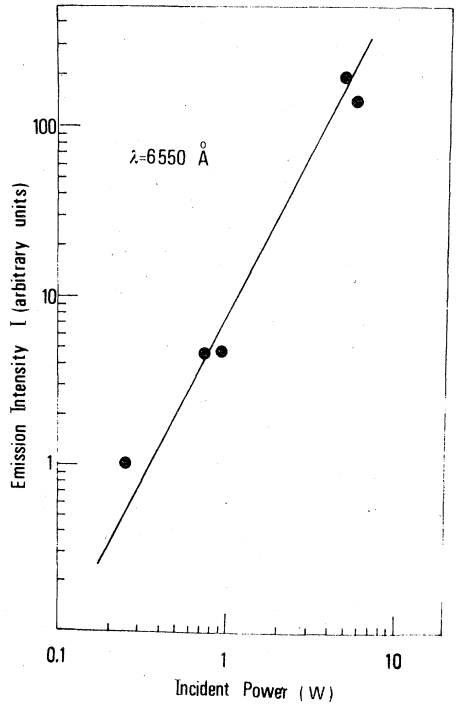

FIG. 6. Emission intensity of the N_1 centers as a function of the incident power. The slope of the full line shows the theoretical (quadratic) dependence of the emission intensity on the incident power for a two-photon process [see text, Eqs. (2) and (3)].

emission of the F_3^+ center and its excitation spectrum reflects the F_3^+ absorption bands.[6] The 660-nm emission band is due to N_1 centers. One-photon excitation of the N_1 centers at 560 nm produces the same emission band with the same bandwidth. A different luminescence band in the same spectral region, but with narrower halfwidth, is due to M centers.[9] However, the emission we detected, was not related to the concentration of the M centers, but only to that of the N_1 centers, as measured from the absorption bands.

The two bands centered around 500 and 775 nm appear with greatly varying intensities in all the crystals we have studied. Their intensities are not clearly related to any absorption band. In the initial stages of laser excitation the 500-nm emission grows at the expense of the 775-nm band. The position of the former band changes from 500 nm in the OH^--doped samples to 515 nm in the pure samples. The excitation spectrum of the 775-nm band is very broad covering all the visible and the uv region of the spectrum and showing some structure corresponding to the F and F-aggregate centers. We have not been able to make a precise assignment for the origin of the 500- and 775-nm band and we are continuing the research in this direction.

IV. DISCUSSION

From the measured number of photons emitted (Figs. 3 and 4) one can derive the two-photon absorption cross section with the following considerations. The attenuation dI of a light beam traversing a thickness dz of a sample containing N absorbing centers/cm^3 is related to the linear $\sigma^{(1)}$ and quadratic $\sigma^{(2)}$ absorption cross section as follows:

$$\frac{dI}{dz} = -\sigma^{(1)}NI - \sigma^{(2)}NI^2 . \tag{1}$$

In our experiment, we deduced the number of photons absorbed from the measured number of photons emitted, which is related only to the quadratic process $\sigma^{(2)}$. Moreover the change in intensity is very small, as we checked measuring the laser power before and after the sample, and therefore I is nearly constant. For a sample of thickness l, integration of Eq. (1) gives

$$-\Delta I_{\text{abs}}/l = \sigma^{(2)}NI^2 . \tag{2}$$

Emitted and absorbed photons (I_{em} and ΔI_{abs} respectively) are related by

$$I_{em} = \eta \tfrac{1}{2} (\Delta I_{abs}) . \quad (3)$$

The factor 2 derives from the quadratic absorption. We have assumed for the emission quantum yield η, the same value we have measured for the one-photon processes: $\eta_{N_1} = 0.25$, $\eta_{F_3^+} = 0.46$. The assumption is justified by the fact that the levels excited by the one-photon and two-photon transitions are either the same or very close together, making unlikely the opening of new nonradiative channels for the deexcitation.

From Eq. (2) we obtained the following values for the two photon absorption cross section at 1.06 μm[10]:

$$\sigma^{(2)}_{F_3^+} = 6.5 \times 10^{-49} \text{ cm}^4 \text{ sec photon}^{-1} \text{ center}^{-1} ,$$
$$\sigma^{(2)}_{N_1} = 5.5 \times 10^{-48} \text{ cm}^4 \text{ sec photon}^{-1} \text{ center}^{-1} . \quad (4)$$

The dispersion around the average values of $\sigma^{(2)}$ measured in different crystals is $\pm 50\%$ but, because of the uncertainty of the absolute calibration and of oscillator strength and quantum efficiency of the centers, we estimate that the two-photon cross section given above are probably accurate only with a factor of 2.

Few theoretical studies have dealt with the electronic wavefunctions of the F_3^+ or N_1 centers.[11] The spatial symmetry of the N_1 center, as deduced from piezo-optic and electro-optic measurements[12,13] is C_{2h} and therefore the transitions responsible for the two-photon absorption can be

$$A_g \rightarrow A_g \quad \text{or} \quad A_g \rightarrow B_g .$$

A way to distinguish between these two possibilities is the measurement of the polarization dependence of the two photon excitation.[14] In our experiment, the emission of the N_1 band at 660 nm, excited with two linearly polarized photons is about 70% larger than that excited with two right-hand circularly polarized photons. This behavior can only be attributed[14] to a transition toward a state with the same full symmetry of the ground state. Thus the transition we are dealing with is $A_g \rightarrow A_g$.

The F_3^+ center has C_{3v} symmetry[15] and therefore, not having the inversion symmetry, the same levels can be reached both with a one-photon or two-photon transitions. Because the F_3^+ absorption band, due to the $A \rightarrow E$ transition, peaks at 2.2 eV close to twice the laser energy (2.34 eV) we suppose that the same levels are connected by the two-photon process.

V. CONCLUSION

The results of this work show that the two-photon absorption techniques can be successfully extended to the study of color centers. Indeed we have measured, for the first time, the two-photon absorption cross sections of the N_1 and F_3^+ centers in NaF.

These results could be greatly extended with the availability of an ir tunable laser that will make possible the measurements of the two-photon absorption spectra as a function of wavelength. In this way we hope that the present knowledge of the electronic structure of color centers will be broadened, particularly with new results concerning the even parity excited states of centrosymmetric centers.

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[1] H. Mahr, in *Quantum Electronics*, edited by C. L. Tang (Academic, New York, 1976), Vol. 1A, p. 285.
[2] J. M. Worlock, in *Laser Handbook*, edited by F. Arecchi and S. DuBois (North-Holland, Amsterdam, 1972), Vol. 2, p. 1323.
[3] D. Fröhlich and M. Sondergeld, J. Phys. E 10, 761 (1977).
[4] W. Kaiser and C. G. B. Garrett, Phys. Rev. Lett. 7, 229 (1961).
[5] A. Chandra, J. Chem. Phys. 51, 1499 (1969).
[6] K. Erlasser and H. Seidel, Phys. Status Solidi B 43, 305 (1971).
[7] A. Chandra and D. F. Holcomb, J. Chem. Phys. 51, 1509 (1969).
[8] M. Casalboni, U. M. Grassano, and A. Tanga, Optics Commun. 23, 95 (1977).
[9] P. Podini, Phys. Status Solidi 9, 737 (1965).
[10] The values of the cross sections (4) are different from those quoted in a preliminary report of this work (International Conference on Defect in Insulating Crystals, Gatlinburg, Tennessee, 1977, Abstract, p. 66). This is due to the direct measurement of the quantum efficiency η and to a better absolute calibration of the detection system.
[11] Shao-Fu Wang, Phys. Rev. 147, 521 (1966).
[12] A. E. Hughes and W. A. Runciman, Proc. Phys. Soc. Lond. 86, 615 (1965).
[13] A. A. Kaplyanskii, V. N. Medvedev, and A. P. Skvortsov, Opt. Spectrosc. 35, 382 (1973).
[14] W. M. McClain, J. Chem. Phys. 55, 2789 (1971).
[15] L. F. Stiles and D. B. Fitchen, Phys. Rev. Lett. 17, 689 (1966).