Production of Stabilized Coloration in Alkali Halides by a Two-Photon Absorption Process

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We have measured the stabilized coloration produced from the conversion of U centers in KCl by means of a two-photon process. The measurements show that the coloration involves energy transfer via electron-hole pairs, rather than direct photoexcitation of the U centers. The absolute two-photon absorption cross section of KCl at $\lambda = 266$ nm was determined.

We have demonstrated, for the first time, an efficient, two-photon, room-temperature process for the production of stabilized coloration in the alkali halides. The process involves the conversion of U centers[1] to essentially permanent F centers, as a result of a two-photon excitation. By taking advantage of the large penetration depth of two-photon absorption, and the well-controlled optics of laser beams, we have been able to study the detailed dynamics of the process. The results show that the conversion proceeds by energy transfer from electron-hole pairs photoproduced from the crystal host, rather than by direct photoexcitation of the U centers. We also obtain an absolute value for the two-photon absorption cross section of KCl at $\lambda = 266$ nm.

The two-photon process not only provides information on the basic physics of the U-to-F conversion, but it is also of interest as a new technique for the production of stable color centers. In recent years such centers have been used as the basis for various photochromic[2] and laser devices.[3] The use of a spatially coherent laser beam to initiate the conversion offers a number of interesting new possibilities such as the production of a distributed-feedback F_A-center laser.[3,4] It is significant that the only requirement on the photon energy is $\frac{1}{2}E_g < h\nu < E_g$, where E_g is the alkali-halide band gap; thus the process can be used with U centers in any alkali-halide host, by using various known uv laser sources.

Previously, two-photon absorption cross sections have been determined only for alkali halides of band gap smaller than the range of the chlorides.[5,6] The production of coloration by a two-photon process in alkali halides containing no U centers has also been reported,[7] and has recently been studied in some detail by Bradford, Williams, and Faust.[8] However, in such pure crystals the produced coloration (which results from the decay of self-trapped excitons) is largely transient.

The conversion of U centers to stabilized F centers via single-photon processes, using x rays[9] or uv light,[10] has been known for some time, but the dynamics have not been fully investigated or interpreted. We find that published data from x-ray experiments[9] can also be fitted by the same basic model of exciton-induced $U\rightarrow F$ conversion that we have used to explain our data. (The extremely short penetration depths encountered in the uv experiments make their interpre-

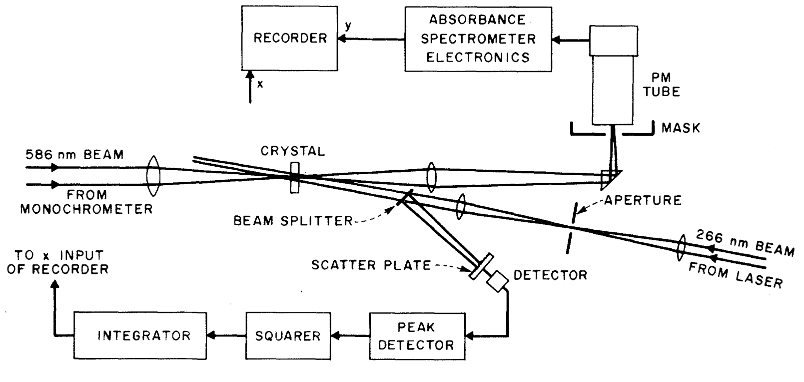

FIG. 1. Schematic diagram of the apparatus.

tation difficult.[10])

Our experimental apparatus is shown in Fig. 1. Intense pulses of light at λ = 266 nm [the fourth harmonic of a Nd:YAlG (yttrium aluminum garnet) laser system,[11] fourth-harmonic pulse energy ~1 mJ, duration ~8 nsec, repetition rate ~5/sec], after passing through an ~5%-transmitting spatial filter, impinged on a KCl crystal ($T = 300°\mathrm{K}$) containing U centers of initial concentration U_0. The beam had a Gaussian intensity profile with radius (e^{-2} intensity) of 0.26 mm at the crystal, and produced a readily observable colored spot. Growth of the F-band absorption was continuously monitored with a special dual-beam absorption apparatus described elsewhere.[12] At the crystal the monitor beam had a square cross section about 60 μm on each side; thus only the uniformly colored center of the spot was measured. Additionally, a small sample of the 266-nm light was detected, and an electrical signal representing the energy in each pulse obtained. Those signals were then squared and integrated, yielding an analog of the quantity

$$\epsilon' = \sum_i \left[\int I_i\, dt\right]^2. \tag{1}$$

As long as the pulse shapes remain constant in time, ϵ' is directly proportional to the true two-photon exposure

$$\epsilon = \sum_i \int I_i^2\, dt. \tag{2}$$

Figure 2 shows a typical curve of coloration versus two-photon exposure. Following an initial steep rise whose slope is essentially independent of U_0 for $U_0 \gtrsim 1\times10^{17}$ cm^{-3}, the curve bends over and finally saturates at an optical density determined by U_0 and by the mean intensity I of the uv light pulses. For each crystal the initial portion of the curve was independent of the mean pulse intensity, verifying that the initial coloration results from a two-photon process. (Note that in all our experiments the samples were always optically thin for the laser beam.)

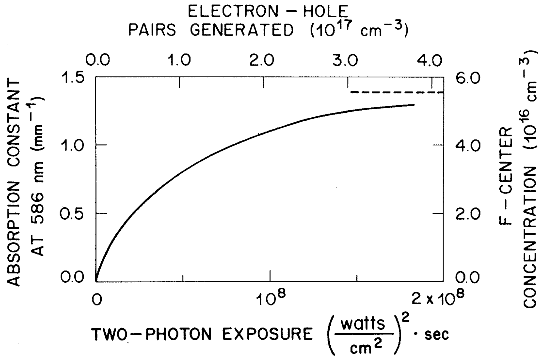

FIG. 2. Induced absorption at 586 nm, as a function of two-photon exposure, for a 0.63-mm-thick Li-doped KCl crystal initially containing 1.3×10^{17} U centers/cm^3. The dashed line represents the best-fitting saturation coloration. Approximately 10^4 laser pulses were required to produce this curve.

The model we propose to explain the curve of Fig. 2 is the following: First, two-photon absorption by the lattice produces electron-hole pairs. These may recombine at a U center, at an F center, or directly in the lattice. In the first instance,[13] the energy released upon electron-hole annihilation serves to convert the U centers into F centers with 100% quantum efficiency.[14] Our model also allows for the existence of the reverse process (resulting from annihilation at an F center) with a certain (unknown) efficiency η. Thus, the time-average behavior of the coloration process should be governed by the equation

$$\frac{dF}{dt} = N\frac{\sigma_U U - \eta\sigma_F F}{\sigma_U U + \sigma_F F + \sigma_L L}, \tag{3}$$

where N is the number of electron-hole pairs generated per cubic centimeter per second; F, U, and L are the F-center, U-center, and halide-ion densities, respectively; and σ_U, σ_F, and σ_L represent the relative rate coefficients for electron-hole annihilation at U centers, F centers, and halide ions, respectively. The general solution to Eq. (3) is

$$F(1-\beta) - \left[\frac{(1+\eta)\beta}{1+\eta\beta}U_0 + \gamma\right]\ln[1-(1+\eta\beta)F/U_0] = (1+\eta\beta)Nt, \tag{4}$$

where $\beta \equiv \sigma_F/\sigma_U$ and $\gamma \equiv \sigma_L L/\sigma_U$. (It is assumed that $F + U = U_0$.) For $F/U_0 \ll 1$, Eq. (4) reduces to

$$F \cong Nt/(1+\gamma/U_0), \tag{5}$$

whereas, for very long times, Eq. (4) becomes

$$F \cong [U_0/(1+\eta\beta)][1-\exp(-\Gamma N t)], \tag{6}$$

where Γ is a function of η, β, γ, and U_0.

Strictly speaking, the above model is not yet complete. In the first place, it neglects the creation of F centers from decay of self-trapped excitons.[8] However, as noted above, the F centers created in this way are largely unstable, and, in any event, the term to be added would be important only in the limit of very low U-center concentration. Second, we have observed that change in the mean pulse intensity is accompanied by change in the saturation coloration. Thus, to the right-hand side of Eq. (3) should be added a term $-\sigma_F'\eta' FI/\hbar\omega$, where σ_F' is the single-photon absorption cross section at $\lambda = 266$ nm, I the mean intensity, and η' the quantum efficiency for the back process $F \rightarrow U$. At the intensities used in most of our experiments, for example in Fig. 2, this term reduced the saturation coloration by as much as a factor of 2. However, at the highest intensities employed by us ($I \sim 20$ MW/cm^2), the rate for the two-photon process is large enough that the single-photon process can be neglected.

There is one more single-photon effect that is of importance when the coloration is carried out at temperatures near 300°K. Photoionization of the F centers by the uv beam initiates the well-known aggregation process,[15,16] which, in a pure crystal, converts them to F_2 and higher aggregate centers. To avoid that complication, our samples were heavily doped with Li (0.1%). As is also well known, the exclusive end product of the aggregation is then F_A centers.[16] The $F \rightarrow F_A$ conversion was essentially instantaneous on the time scale of our experiments, and we also chose a monitor wavelength ($\lambda = 586$ nm), for which the F and F_A absorption cross sections are the same.

According to Eq. (5), the initial slopes of the coloration curves will be independent of U_0 when $U_0 \gg \gamma$. By contrast, for a model involving direct photoexcitation of the U centers, the initial slope would always be directly proportional to U_0. (Note that these slopes are not affected by any back process.) Our experimental results for the initial slopes, for various crystals with different values of U_0, are plotted in Fig. 3. The best fit to the behavior implied by Eq. (5) was obtained for $\gamma = 4 \times 10^{16}$ cm^{-3}. The deviation from the theoretical curve near $U_0 = 0$ corresponds to the neglect, in Eq. (3), of the creation of F centers from self-trapped excitons. Nevertheless, the results agree with the model of Eq. (3), and conclusively show that direct photoexcitation of the U centers is not involved to any significant extent.

The exposure ϵ was calibrated in absolute units through coordinated measurements of the mean laser power, the laser-pulse duration, the intensity profile of the uv beam, and the number of pulses required for a given recorded displacement along the x axis (ϵ' axis). The average laser pulse energy was measured with an Eppley thermopile placed just ahead of the crystal. A careful measurement of the initial slope of the coloration curve for a crystal containing a large density of U centers ($U_0 > 10^{18}$ cm^{-3}) then yielded N/ϵ, from which we obtained the value

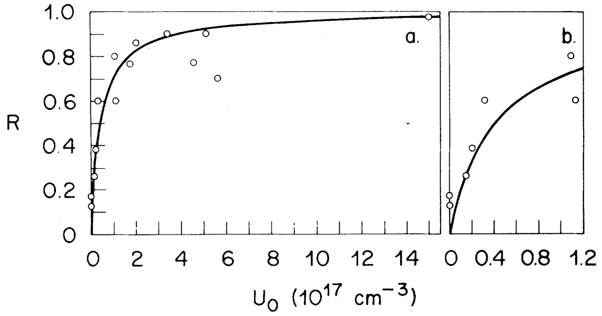

FIG. 3. Experimental results for the relative initial slopes (R) of the curves of coloration versus two-photon exposure for various values of U_0. (a) Complete data. (b) Detail of low-concentration region. (The slopes have been normalized to $R = 1$ for $U_0 = \infty$.) The solid line is a theoretical curve, calculated for $\gamma = 4.24 \times 10^{16}$ cm^{-3}.

$$\sigma_2 = 7 \times 10^{-50} \text{ (cm}^4\text{ sec/photon)/KCl molecule}$$

for the two-photon absorption cross section at $\lambda = 266$ nm. By far the largest source of error in this result stems from fluctuations of the temporal structure of the laser pulse from the assumed Gaussian shape, and leads to an uncertainty in the above number on the order of a factor of 2.

Prolonged exposure to the highest intensities available to us produces a 50% or better conversion of $U \rightarrow F$, as determined both from the coloration produced and from measurements of the decline of the U band. We thus infer that $\eta\beta < 1$ [note Eq. (6)], and that for large U_0 the initial curvature of the coloration curves will depend almost exclusively on β and U_0. By a careful fitting to the initial curvatures, we obtain $\beta = 8 \pm 2$. From the saturation behavior of the curves we obtain the limits 2×10^{-22} cm$^2 < \sigma_F'\eta' < 9 \times 10^{-22}$ cm^2, where the lower limit corresponds to assuming $\eta\beta = 1$, and the upper limit to $\eta\beta = 0$. As indicated above, we have also made an excellent fit of Eq. (4) to existing x-ray coloration data on KBr,[9] obtaining $\beta \simeq 7$, and $\eta\beta \leq 0.1$.

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[1] The U center consists of an H$^-$ ion trapped at an anion vacancy. For a brief introduction to U centers and associated references, see W. B. Fowler, in *Physics of Color Centers,* edited by W. B. Fowler (Academic, New York, 1968), Chap. 2, p. 123.

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Lett. 22, 299 (1973).

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[4] As a first step toward the production of such lasers we have made thick holographic gratings ~10 mm long, several mm wide, and several mm thick.

[5] J. J. Hopfield and J. M. Worlock, Phys. Rev. 137, A1455 (1965).

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[9] W. Martienssen and H. Pick, Z. Phys. 135, 309 (1953).

[10] M. Ueta, M. Hirai, and H. Watanabe, J. Phys. Soc. Jpn. 15, 593 (1960).

[11] Holobeam, Inc., Paramus, N. J., model 500 QUV.

[12] L. F. Mollenauer and D. H. Olson, Rev. Sci. Instrum. 46, 677 (1975).

[13] There are two possibilities here. Either (1) the electron is trapped first by the *U* center, and the hole catches up with it later, or (2) the electron may be temporarily trapped elsewhere, and the hole directly annihilates an electron of the *U* center. In any event, the net accounting entering into Eq. (3) is the same; i.e., for every electron-hole annihilation occurring at a *U* center, one $U \to F$ conversion takes place. The detailed dynamics of the electron-hole motion and trapping is probably similar to that described recently for KI and NaI. [H. B. Dietrich, A. E. Prudy, R. B. Murray, and R. T. Williams, Phys. Rev. B 8, 5894 (1973).]

[14] It has been shown that the $U \to F$ conversion by excitons produced by a single-photon excitation occurs with 100% quantum efficiency (see Ref. 10). There is no reason to expect a different efficiency here.

[15] H. Härtel and F. Lüty, Z. Phys. 177, 369 (1964).

[16] F. Lüty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), Chap. 3.

Metamagnetic Behavior of Triethylenetetrammonium Hexachlorocuprate(II), $[C_6H_{22}N_4]CuCl_6$

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The compound triethylenetetrammonium hexachlorocuprate(II), $[C_6H_{22}N_4]CuCl_6$, exhibits two-dimensional magnetic behavior in the temperature range 20–75 K with an exchange constant of $J/k = 19.4$ K derived from a fit of the data by the expansion of Baker *et al.* There is a phase transition to an antiferromagnetic state at 8.95 ± 0.1 K, and the magnetization data suggest metamagnetic behavior.

Metamagnetic behavior in transition-metal antiferromagnets is a phenomenon that has been known both theoretically and experimentally for sometime. In all analyses of this field-dependent behavior, Ising-like properties have been ascribed to the ground state of the ion in question. This has been a natural consequence of having to account for the required anisotropy.

Generally anisotropy arises from single-ion (crystal-field) effects, dipole-dipole considerations, and anisotropic exchange interactions. Until this report, metamagnetism had been found only in compounds where the anisotropy was a result of crystal-field effects within the ground-state manifold, i.e., in compounds containing Fe(II), Co(II), Ni(II), and Dy(III). Here we give a preliminary report of the metamagnetism in triethylenetetrammonium hexachlorocuprate(II), henceforth $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$. This is the first Cu(II)-containing compound to be described which exhibits metamagnetism. It is especially intriguing that the magnetic behavior of the compound could not have arisen from single-ion effects.

Polycrystalline $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ was prepared from a 1:1 mole ratio of triethylenetetrammonium chloride, previously prepared by titration of the amine in ethanol, and $CuCl_2 \cdot 2H_2O$ in an HCl-H_2O solution. Although single crystals are exceptionally difficult to obtain, a few platelike crystals were obtained. These were examined by x rays, and the preliminary results indicate that the material is either hexagonal or more likely monoclinic with $\beta = 120°$ and with suc-