RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 4 15 AUGUST 1985

Total transformation of electronic F-center emission into multiple-state CN^- vibrational emission (4.8 μm) in CsCl

Yihong Yang, Wolf von der Osten, and Fritz Lüty
Physics Department, University of Utah, Salt Lake City, Utah 84112

(Received 1 May 1985)

Optical excitation of a new F-center–CN^- defect complex in CsCl produces—instead of any electronic emission—a highly efficient five-band vibrational emission around ≈ 4.8 μm (≈ 0.25 eV), involving the five lowest states of the CN^- anharmonic oscillator. Pulsed laser excitation shows that the energy transfer from the excited F electron occurs mainly at 1 eV into the fourth CN^- level, producing a sequence of $\Delta n = 1$ population inversions and emissions with great potential for laser application. $\langle 100 \rangle$ polarization of the CN^- emission reveals rotational alignment of the CN^- molecule by the associated F center.

The simplest O_h symmetry electronic defect in ionic crystals—the F center—can be associated with a great variety of cationic, anionic, or vacancy-point (or pair) defects. These F aggregate centers of reduced local symmetry, changed wave functions, and electron-lattice coupling[1] share one common feature with F centers, i.e., highly efficient, spectrally broad, and Stokes-shifted electronic emission bands. Several of these systems (like F_A, F_B, F_2^+, F_2^- centers) have gained significance as solid-state systems capable of tunable near-ir laser emission.

A new optical property can be introduced by associating F centers with substitutional diatomic molecular defects. The first realization[2] of this, an F-center–CN^- defect pair on (NNN) $\langle 110 \rangle$ positions [F_H (CN^-) defect] in KCl, shows an electronic-absorption and emission band of similar strength and only slight spectral broadening and red shift compared to the F center. As a new effect, however, it displays a very weak energy transfer from the excited F electron to the CN^- internal stretching mode ($E_{\text{vibr}} = 0.25$ eV), leading to $n = 0 \rightarrow 1$ excitation and subsequent $m = 1 \rightarrow 0$ radiative relaxation of this CN^- mode.[2] Though this produced the first discovery of molecular vibrational fluorescence in ionic solids, the weak coupling of the CN^- to the optical F-center excitation (at $E_{\text{abs}} = 2.3$ eV) allowed only low quantum efficiency ($\eta \approx 0.04$) and a low energy-conversion rate $\eta_E = \eta E_{\text{vibr}}/E_{\text{abs}} \approx 4 \times 10^{-3}$ from visible pumping into infrared emission light.

We report here—after a systematic search—a new $F_H(CN^-)$ center in CsCl with a dramatic increase in the F-electron–CN^- vibrational coupling and great application potential. Unlike the NaCl structure of KCl, the body-centered cesium halide structure should produce for a next-nearest-neighbor (NNN) F-CN^- pair a $\langle 100 \rangle$ oriented complex as illustrated in Fig. 1. As for F_A centers in KCl, one can expect that the excited F-center $2p$ state could split into two spectrally separate absorption transitions [$F_H(1)$ and $F_H(2)$], polarized parallel and perpendicular to the pair axis.

Our first experiments confirm this [Fig. 2(a)]: CsCl crystals containing low (6×10^{-5} to 6×10^{-3}) mole ratios of CN^- defects, when additively colored, quenched and cooled, show essentially only the well-known F absorption band (with its characteristic spin-orbit split spectral structure). Irradiation into the F band around 170 K leads to conversion into two absorption bands (0.27-eV separation), which we attribute to migration and association of the F centers with CN^- defects, forming the $F_H(CN^-)$ center as illustrated in Fig. 1. The most dramatic effect of this $F \rightarrow F_H(CN^-)$ conversion occurs in optical emission, as shown by excitation spectra in both stages [Fig. 2(b)]. The normal F emission at 1.25 eV observed in the quenched state[3] becomes totally suppressed by $F \rightarrow F_H$ conversion, and is replaced by a much stronger emission around 4.8 μm (excited in both F_H absorption bands). In both stages the emissions were measured with broad bandpass filters (peaking around 1.0 and 4.8 μm) and with an InSb detector. From these conditions and the observed relative emission strength, we estimate that the F_H liminescence quantum efficiency η must be considerably higher ($\sim$4–6 times) than the η value of the F luminescence.

Figure 3 shows the F_H (CN^-) emission spectra in CsCl containing 6×10^{-5} and 6×10^{-3} mol ratio CN^-, both measured at two temperatures. For the low-CN^--concentration case we obtain five about equally separated emission bands, all shifted to lower energies compared to the indicated position of the $n = 1 \rightarrow 0$ emission of the isolated CN^- defect [Fig. 3(a)]. As the band separation $\Delta\nu \approx 25$ cm^{-1} corre-

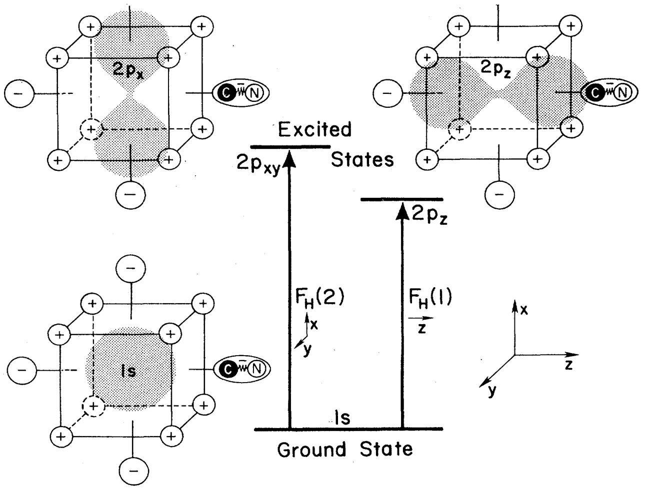

FIG. 1. Structural model, wave functions, and energy levels of the ground and excited states of the $F_H(CN^-)$ center in cesium halides.

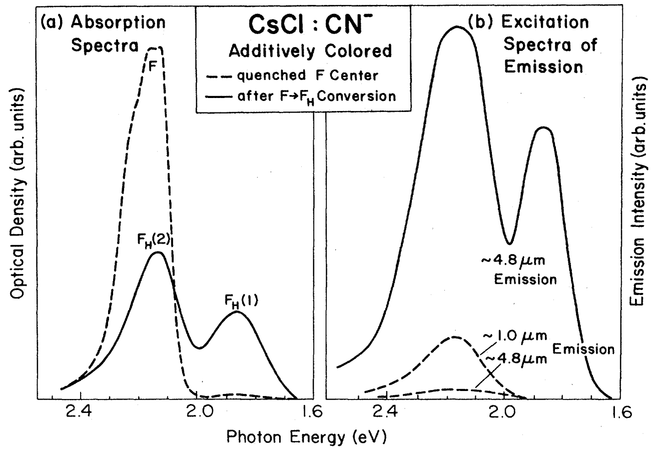

FIG. 2. Optical-absorption spectra (a) and emission excitation spectra (b) of additively colored CsCl:CN$^-$; quenched (— — —), and after $F \rightarrow F_H(\mathrm{CN}^-)$ center conversion (——).

sponds to the anharmonicity shift among the CN$^-$ oscillator states, we interpret the five emission bands as the $\Delta n = 1$ transition among the six lowest energy CN$^-$ vibrational states of the $F_H(\mathrm{CN}^-)$ center. The five-band structure remains resolved at higher temperatures (at least to $T = 120$ K), and the emission strength decreases only gradually over this temperature range, in contrast with the rapid temperature decrease of the normal F emission in CsCl.[3]

For the high-CN$^-$-concentration case [Figs. 3(c) and 3(d)], the 15-K emission spectrum looks similar, but contains an added extra band at the spectral position of the isolated CN$^-$ defect emission. Modest temperature increase [to 36 K in Fig. 3(d)] produces a strong decrease of the F_H center emission bands (particularly for the low n value transtions), combined with increase of the isolated CN$^-$ defect $n = 1 \rightarrow 0$ emission band. Obviously, for high CN$^-$ defect densities the excitation of the CN$^-$ in the F_H (CN$^-$) complex can efficiently transfer—with the help of thermal activation energy—its energy into the abundant isolated CN$^-$ defect system. Migrating by resonance energy transfer[4] through this system, the CN$^-$ excitation can be transported to some trap with a radiationless deexcitation channel (e.g., a CN$^-$ defect pair[5]), resulting in a quick decay and disappearance of the $F_H(\mathrm{CN}^-)$ emission with increasing temperature. Evidently, the dilute case of noninteracting $F_H(\mathrm{CN}^-)$ and isolated CN$^-$ defects has a much more simple, powerful, and temperature-independent behavior compared to the concentrated CN$^-$ "interactive case."

The symmetry of the $F_H(\mathrm{CN}^-)$ complex was determined by polarized measurements (Fig. 4), performed in CsCl:CN$^-$ crystals oriented by x-ray diffraction to a ⟨100⟩ orientation. [100] polarized excitation in the $F_H(1)$ band produces nearly completely parallel [100] polarization of the CN$^-$ emission, preserved essentially under increase of temperature to 70 K. The same [100] excitation of the $F_H(2)$ absorption leads to strong perpendicular [010] polarization of the CN$^-$ emission. These two polarized measurements confirm the model illustrated in Fig. 1.

(a) ⟨100⟩ orientation of the F-CN$^-$ complex, with $F_H(1)$ and $F_H(2)$ absorptions polarized parallel and perpendicular to the ⟨100⟩ axis, respectively.

(b) The CN$^-$ molecule (a weakly hindered rotor in the isolated defect case) is aligned along the ⟨100⟩ pair axis by strong interaction with the neighboring F center—even up to high temperatures.

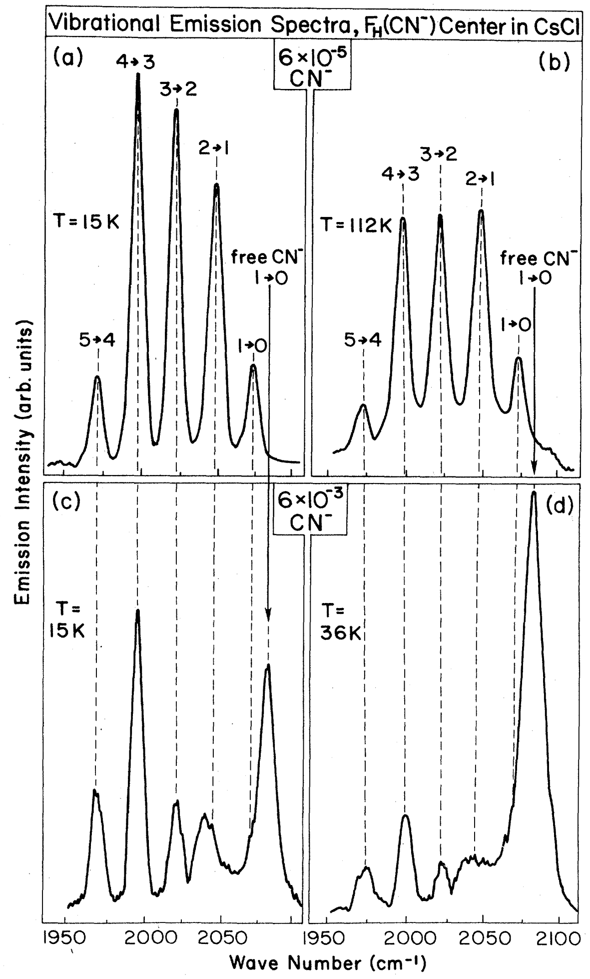

FIG. 3. Emission spectra of $F_H(\mathrm{CN}^-)$ defects in CsCl with the two indicated CN$^-$ concentrations, both measured at two low temperatures under 580-nm dye-laser excitation.

In Fig. 5(a) we summarize the measured time dependence of five $F_H(\mathrm{CN}^-)$ emission bands after excitation with a 40-nsec excimer-laser-pumped dye-laser pulse. The high-level emissions ($n = 5 \rightarrow 4$ and $4 \rightarrow 3$) start immmediately and decay rapidly. The emissions from the lower levels occur with small initial value, but mostly in delayed buildup (by transitions from the higher levels) and subsequent slow emission decay. In Fig. 5(b) we plot the relative size of the $t = 0$ initial emission with bars for all excited states, illustrating their direct pump probabilty through coupling to the electronic excitation. Obviously, pumping occurs with a distribution with a strong peak at the fourth state ($4E_{\mathrm{vibr}} \approx 1.0$ eV), indicating a very high quantum efficiency of $\Delta n = 1$ vibrational emission ($\eta \approx 4$) and energy conversion efficiency $\eta_E = \eta E_{\mathrm{vibr}}/E_{\mathrm{abs}} \approx 0.5$.

In the present emission measurements (Figs. 3, 4, and 5), the pump-light intensity used was low enough to excite $F_H(\mathrm{CN}^-)$ centers only with their CN$^-$ in the vibrational ground state. Under considerably increased pump-light in-

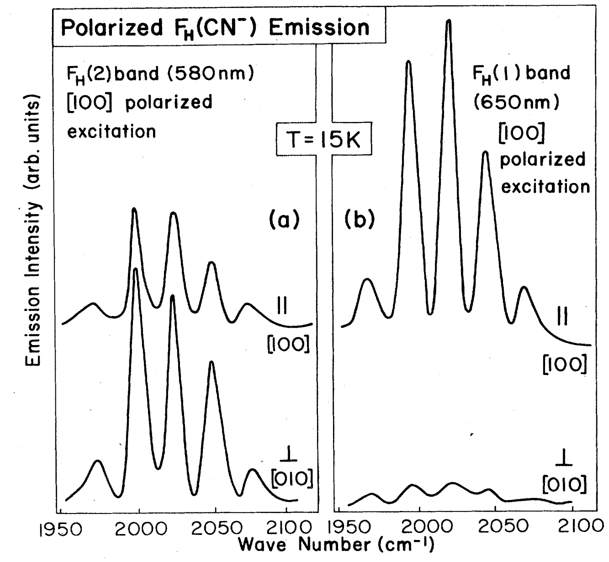

FIG. 4. $F_H(CN^-)$ emission spectra in $CsCl+3\times10^{-4}$ CN^- under [100] polarized excitation in the $F_H(2)$ and $F_H(1)$ band, measured parallel and perpendicular to the excitation polarization.

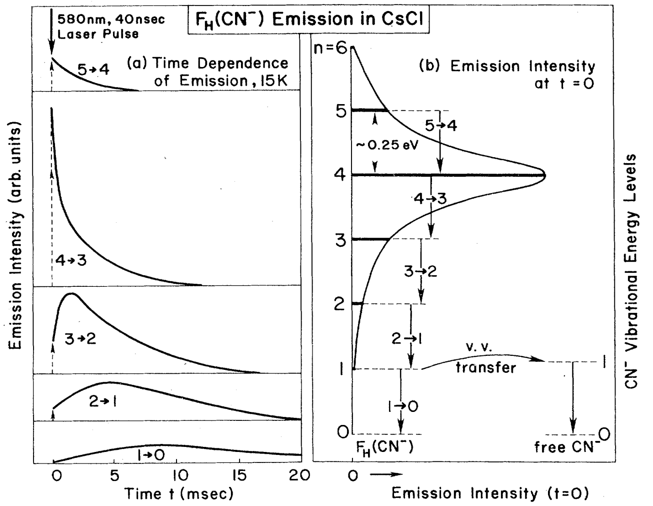

FIG. 5. (a) Time dependence of the emission intensity in the five $F_H(CN^-)$ emission bands, after 40-nsec pulsed-laser excitation. (b) Emission intensity from the five lowest excited CN^- vibrational states, immediately after pulsed $F_H(CN^-)$ electronic excitation, plotted into level diagram.

tensity (focused cw laser), however, repeated F_H excitation can occur prior to the slow CN^- relaxation in the F-CN^- complex. This leads to partial pumping of "vibrationally excited F_H centers" into higher CN^- levels, as we could observe by a relative increase of the 5 → 4 emission and an appearance of a higher 6 → 5 emission band in spectal measurements of the type in Fig. 3.

Figure 5 illustrates directly the population inversion among the CN^- levels achieved under pulsed pumping (strongest between $n=4$ and 3), indicated by the rapid initial decay of the 4 → 3 emission, most likely by stimulated transitions. Experiments with this system for powerful 4.8-μm laser applications are actively under way. They possibly allow laser light tuning by the above described shift of the inversion into higher CN^- levels under strong pump-light intensity.

Efforts to fully understand this highly efficient and novel energy-transfer process between F and CN^- are under way—both theoretically and by further experiments. Resonance Raman measurements of the $F_H(CN^-)$ defects will clearly decide if the F_H-electron–CN^- vibrational coupling occurs in the absorption process itself or during and/or after excited-state relaxation. If the latter is the case, the electronic energy of the normal F emission ($E \approx 1.25$ eV) fits closely to the fourth CN^- vibrational level excitation energy, suggesting a direct and highly efficient transfer process between both. Experiments of F_H centers in CsBr and CsI are already under way.

Support by National Science Foundation Grant No. 81-05332 for this work, and by the Deutsche Forschungsgemeinschaft for one of the authors (W.v.d.O.) is acknowledged.

---

[1] W. B. Fowler, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), Chap. 2.

[2] Y. Yang and F. Lüty, Phys. Rev. Lett. **51**, 419 (1983).

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

[4] H. Dubost and R. Charneau, Chem. Phys. **12**, 407 (1976).

[5] K. P. Koch, Y. Yang, and F. Lüty, Phys. Rev. B **29**, 5840 (1984).