

INFRARED ABSORPTION SPECTRUM OF THE  $F^*$  CENTER IN KI

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Recently there have been reported in the literature a number of theoretical and experimental efforts to understand further the nature of the excited states of the  $F$  center. In an earlier experiment,<sup>1</sup> the absorption spectrum of the first excited state of the  $F$  center (denoted  $F^*$ ) was investigated by populating the  $F^*$  state with a pulsed ruby laser and monitoring the induced absorption in the spectral region from 4 to 0.3 eV. In that experiment, the conventional spectroscopic source used in the infrared region (a Globar) was sufficiently weak that at 0.3 eV the net signal-to-noise ratio approached unity. This prevented investigation further into the low-energy region, where appreciable oscillator strength was expected to reside.<sup>1</sup>

In this Letter we report an extension of this spectroscopic investigation further into the infrared region, an effort made possible by replacing the Globar source with a xenon gas laser.<sup>2</sup> The discrete, essentially untunable lines of a gas laser would not be useful for study of a highly structured absorption spectrum. However, in any spectral region where the absorption varies smoothly (in the continuum, or where discrete states are sufficiently broadened by the strong coupling between the electrons and the lattice) the gas laser may serve well because of its multiplicity of intense lines. Xenon alone covers the 0.62- to 0.096-eV range with ten useful lines.

An additively colored KI crystal (containing typically  $10^{15}$ - $10^{17}$   $F$  centers/cm<sup>3</sup>) was placed in an optical Dewar. The sample Dewar was inserted in the infrared beam between the gas laser and a monochromator. A photoconductive copper-doped germanium detector was used to measure the transmitted infrared light. An unfocused ruby laser with an output of 5 J and a pulse duration of 500  $\mu$ sec was used to excite the  $F$  centers. A set of Corning glass filters and dielectric filters served as a convenient means of attenuating the ruby-laser intensity without otherwise changing the character of the laser pulse. We were able to measure the induced absorption to within 5% of the full infrared signal. We verified that the induced absorption constant was independent of the infrared laser intensity (no bleaching of the  $F^*$

population).

Figure 1 shows the absorption spectrum of the  $F^*$  center at two temperatures (77°K and about 10°K). With appropriate normalization, the plots of the absorption constants versus the excitation intensity at each spectral point can be superimposed, within the experimental error, on a plot of the fluorescence intensity versus the excitation intensity. From this we can confirm that the emission and the absorption processes share a common initial state, i.e., the  $F^*$  state. To establish this point further, a  $Q$ -switched excitation scheme was used, in which the  $F^*$  state was populated in  $3 \times 10^{-8}$  sec. The subsequent time decays of the absorption and of the emission were then measured. We observed time constants of  $(1.9 \pm 0.2) \times 10^{-6}$  sec for the emission and  $(2.1 \pm 0.2) \times 10^{-6}$  sec for the absorption process, which are both in good agreement with a previous lifetime measurement of  $2.2 \times 10^{-6}$  sec.<sup>3</sup>

Concerning the shape of the  $F^*$  absorption spectrum and its over-all magnitude, we make

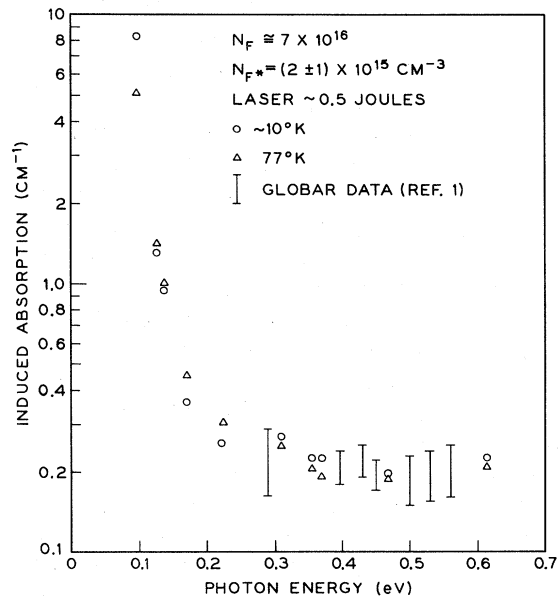


FIG. 1. Absorption spectrum of the  $F^*$  center. Typical errors are  $\pm 10\%$  of the absorption constant, except at the 0.096-eV point, where it is  $\pm 20\%$ . The induced absorption vanishes above 1.0 eV; see Fig. 10, Ref. 1.

the following two observations:

(1) Swank and Brown<sup>3</sup> measured photoconductivity under  $F$ -light irradiation as a function of temperature. The functional form of their data led these authors to attribute the photocurrent to thermal ionization across a gap of 0.11 eV. To the degree of confidence that the thermal ionization energy of the  $F^*$  state can be inferred from this measurement of photoconductivity, and recalling that the photoionization energy should be greater than or equal to the thermal ionization energy (possible Stokes shift), it is reasonable that our data should include points below the photoionization energy. And we may attribute the sharp rise in optical absorption which we observed near 0.1 eV to a transition from the  $F^*$  state to another bound state (or a set of states) below the conduction band. Our data, in fact, give no clear indication of a photoionization edge, presumably because the edge is hidden under the high-energy side of the intense absorption to these bound states.<sup>4</sup> (This phenomenon has, actually, some generality.)

(2) We expected<sup>1</sup> in the low-energy region a substantial increase in the absorption such as that observed, since the requirements of the  $f$ -sum rule were not met in the region studied previously with the Globar (energies greater than 0.3 eV). The area under the absorption curve thus far measured, including high-energy data from Ref. 1, corresponds to an integrated oscillator strength  $1.1 \pm 0.3$ .<sup>5</sup>

Any induced absorption persisting after the excitation pulse can be attributed to absorption by a suitably long-lived species generated by the ruby light (e.g., the  $F'$  center, near 1.8 eV, Ref. 1). Such an absorption was observed in our work. The spectrum is shown in Fig. 2. At 77°K, the state responsible for this absorption is stable for 60 msec or longer. There is a sharp saturation in the population of this state at a ruby-laser power of 1 kW, similar to that of the  $F'$  population at 0.1 kW.<sup>1</sup>

In conclusion, the absorption spectrum of the  $F^*$  center shows a strong, very steep rise near the band edge determined from thermally activated photoconductivity. We speculate that this rise is due to transitions to bound states.

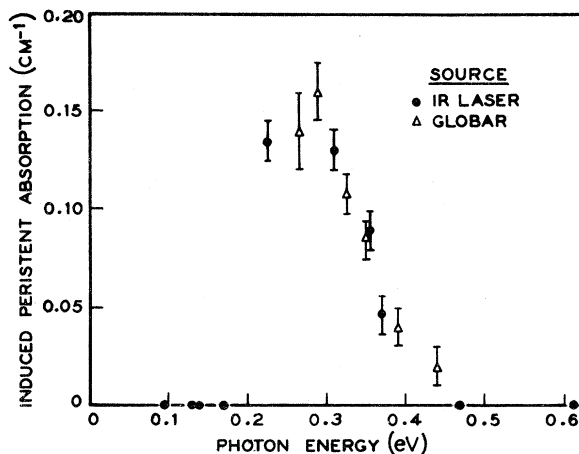


FIG. 2. Absorption spectrum of the newly observed trap at 77°K. The Globar data points are obtained from an earlier run with a different sample. These points contain appropriate normalization.

We observed also a band of persistent absorption at 0.27 eV, which may be due to a new trap.

Two experimentally difficult areas remain for further clarification: First, there should be work to observe structure among the discrete states at still lower energies, where the value of a continuously tunable infrared source would be accentuated. Second, the excitation spectrum of photoconductivity from the  $F^*$  state might in principle reveal the photoionization energy unobscured by the discrete states.

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<sup>1</sup>Kwangjai Park, Phys. Rev. **140**, A1735 (1965).

<sup>2</sup>W. L. Faust, R. A. McFarlane, C. K. N. Patel, and C. G. B. Garrett, Appl. Phys. Letters **1**, 85 (1962).

<sup>3</sup>R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

<sup>4</sup>For discussions and spectra of related systems (shallow impurities in semiconductors), see E. Burstein, G. Picus, B. Hennis, and R. Wallis, J. Phys. Chem. Solids **1**, 65 (1956); and G. Picus, E. Burstein, and B. Hennis, J. Phys. Chem. Solids **1**, 75 (1956).

<sup>5</sup>We have taken  $m_{\text{eff}} = m_0$  in evaluating the oscillator strength from the absorption spectrum.