face region is small because of a cancelation between the transverse and longitudinal fields.[3-5] As a result, the p yield is reduced considerably below the local value as is clear in Fig. 3. This region of small field extends in about 24 Å for $\hbar\omega = 3.78$ eV but decreases sharply as ω decreases. With decreasing ω then, the p yield tends to increase again with the result that $Y_p{}^z/Y_s$ increases. The increase is associated physically with intraband transitions with the momentum transfer, supplied by the longitudinal field, perpendicular to the surface. In the experimental results, this increase extends only to 3.6 eV; in the calculation the increase continues to lower energies. This result suggests that the single-particle intraband effects do act to keep the yield ratio high and it is surface plasmons, not in the calculation, which cause the sharp drop at 3.6 eV. There remains the possibility that the proper joint density of states for intraband transitions has significant structure in this energy range.

We conclude with some comments concerning the efficacy of studying solids by use of the photoemission-into-electrolytes technique. The high values of Y_p/Y_s obtained in our experiments are striking evidence that the electrolyte does not modify the surface character to any appreciable extent. An additional point in this connection is the sharpness of the structure obtained here, as is the fact that the effects of a monolayer on the surface were so apparent.

*On leave from Ames Laboratory-ERDA and Department of Physics, Iowa State University, Ames, Ia. 50010.

[1]See, for example, G. C. Barker, A. W. Gardner, and D. C. Sammon, J. Electrochem. Soc. 113, 1182 (1966).

[2]J. K. Sass, to be published.

[3]K. L. Kliewer, Phys. Rev. Lett. 33, 900 (1974), and to be published.

[4]P. J. Feibelman, Phys. Rev. Lett. 34, 1092 (1975).

[5]J. G. Endriz, Phys. Rev. B 7, 3464 (1973).

[6]See, for example, E. T. Arakawa, R. N. Hamm, and M. W. Williams, J. Opt. Soc. Am. 63, 1131 (1973).

[7]H. Becker, E. Dietz, U. Gerhardt, and H. Angermüller, Phys. Rev. B 12, 2084 (1975); N. E. Christensen, Phys. Status Solidi (b) 54, 551 (1972); N. V. Smith, Phys. Rev. B 9, 1365 (1974).

[8]We use the silver data given by G. B. Irani, T. Huen, and F. Wooten, J. Opt. Soc. Am. 61, 128 (1971).

[9]B. Feuerbacher and N. E. Christensen, Phys. Rev. B 10, 2373 (1975).

[10]P. Zacharias and K. L. Kliewer, to be published.

[11]N. D. Mermin, Phys. Rev. B 1, 2362 (1970).

[12]The escape length for silver in this frequency range is not known. A value in the range of 20–40 Å is reasonable. Note that the exact value is not of great concern here. We are most interested in the shape of the curves.

Nonlinear Optical Excitation of the Relaxed Vibronic States of the F Center in KCl†

F. De Martini,* G. Giuliani, and P. Mataloni
Istituto di Fisica "G. Marconi," Università di Roma, Roma 00185, Italy
(Received 12 August 1975)

We have conducted the first experiment on two-photon excitation of the F center and obtain new and conclusive information about the structure of the relaxed excited states, the strength of electron-phonon interaction, and the amount of vibronic mixing of $|2s\rangle$ and $|2p\rangle$ states, allowing the exact solution of the dynamic problem. A new resonance arising from an additional vibronic mixing ($3s$-$3p$) has been found. The values of the $2s$-$2p$ splitting and of the fluorescence lifetime from $|2p'\rangle$ have been measured for the first time.

We report the first investigation on the relaxed excited states (RES) of the F center in an alkali-halide crystal by a two-photon excitation technique.[1] The structure of the F^* center (F center in RES) in KCl is of particular interest because of the rather complex processes that are found to take place during the crystal relaxation. The experiments of Chiarotti and Grassano,[2] Kuhnert,[3] and Bogan and Fichten[4] have shown evidence that in KCl the $2s$ state, which in absorption lies 0.1 eV above the $2p$ state, crosses the $2p$ state during crystal relaxation and ends up lower in energy.[5] This model is consistent with Bogan and Fichten's assumption that the RES structure consists of nearly degenerate states $|2s'\rangle$ and $|2p'\rangle$ which result from an admixture of the $2s$ and $2p$ states, with $|2s'\rangle$ lower in energy. The exact nature and the strength of the mixing as well as the

validity of the model itself could not be directly ascertained by previous linear-spectroscopy experiments. We believe that a nonlinear method can supply new information on the system and contribute to clarification of its structure.

A 30-nsec, $\lambda = 1.06$-μm pulse generated by a Q-switched Nd-glass laser was focused on the surface of an additively colored KCl crystal (dimensions $1\times1\times1$ cm^3) cooled at liquid-N_2 temperature. The fluorescence arising from the F^* de-excitation to the ground ($1s$) state, following a Franck-Condon (FC) scheme, was detected at 90° by a Baush and Lomb 338625 spectrometer and a 56 CVP photomultiplier. The output signal was suitably gated before being processed by a photon counting technique in order to discriminate against the large number of laser photons scattered into the detection system. During the experiment the laser intensity was kept well under the dielectric breakdown threshold for the crystal.[6] In this respect frequent checks were made with use of clear KCl specimens or with different F-center concentrations N. It has been found that the fluorescence intensity is proportional to N as expected.[1] The crystal was frequently quenched at 700°K with rapid cooling at liquid-N_2 temperature in order to rule out any effect due to centers other than F. The number of fluorescence photons emitted over the entire band in a 4π solid angle and following a 10-kW laser excitation (intensity 100 kW/cm^2) has been evaluated to be 2×10^8 for $N = 1.3\times10^{16}$ cm^{-3}. This figure is in order-of-magnitude agreement with the theoretical results.[1] Details on the two-photon excitation theory in an F-center system will be reported in a following paper.

Two different experiments have been performed at successive times: (a) The two-photon experiment we have just described in which the $1s$ state is selectively coupled in centrosymmetric KCl to the $2s$ state. (b) The one-photon absorption experiment in which coupling occurs to the $2p$ state by resonant excitation of the crystal in the F band, which peaks at 2.3 eV at liquid-N_2 temperature.[7] A nonlinear ammonium-dihydrogen-phosphate crystal inserted in the laser path generated a second-harmonic pulse at $\lambda = 5300$ Å (2.34 eV).

The insertion of the nonlinear crystal and of a Shott BG18 (green) filter in the laser path were the only changes we introduced between the two sets of measurements. The one- and two-photon resonance conditions were approximately satisfied because of the large linewidths (~0.1 eV) of the nearly degenerate $2s$ and $2p$ states.[2] Experiment (b) is similar to the one on the measurement of the F-center laser gain in KCl that we have recently reported.[8] In Fig. 1 the fluorescence spectra obtained in experiments (a) and (b) are shown. In the two-photon experiment the peak power of the laser was 10 kW with an intensity of 10 kW/cm^2 while in the one-photon case the peak power and intensity of the second-harmonic pulse were approximately 100 times less. The one-photon spectrum reproduces the well-known fluorescence spectrum of the F center[7] while the two-photon spectrum is here reported for the first time.

Figure 1 shows a marked energy displacement between the two spectra corresponding, in the case of vertical alignment in the FC diagram of the minima of the potential walls from which the fluorescence occurs, to a large energy splitting $E_{sp} = 0.052$ eV between the corresponding relaxed states. The lack of any apparent interference between the two spectra (no bumps appear in the one- and two-photon bands, respectively, at λ ~0.96 and ~1 μm) is also physically significant as it shows the following: (a) The probability of

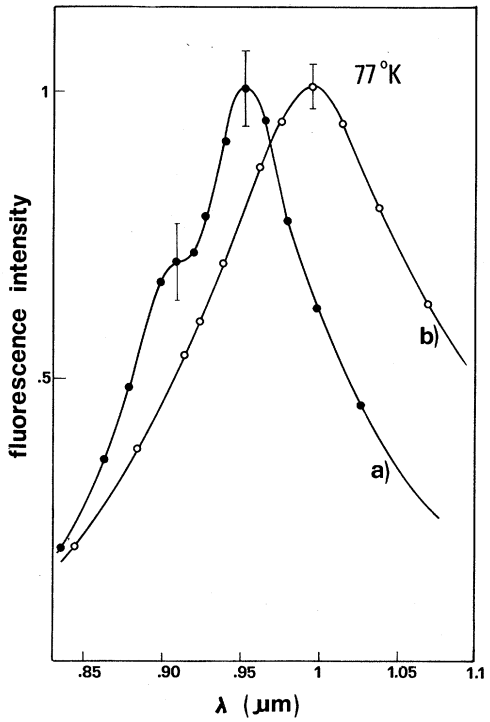

FIG. 1. Fluorescence spectra obtained in a two-photon absorption experiment (curve *a*) and in a one-photon absorption experiment (curve *b*). The two spectra are normalized to the same height. (F-center concentration $N = 1.3\times10^{16}$ cm^{-3}.)

radiative decay from the two-photon–populated RES, referred to as the $|2p'\rangle$ state, is much larger for a transition to $|1s\rangle$ than to the nearby $|2s'\rangle$. Apart from the different values of the corresponding electric-dipole matrix elements, this effect may be simply understood on the basis of the dependence of the spontaneous emission probability on the transition frequency.[9] (b) The number of nonradiative transitions occurring between the states $|2s\rangle$ and $|2p\rangle$ during the crystal relaxation is surprisingly small in spite of the presence of an intense LO phonon field.

The two-photon spectrum shows the evidence of an additional transition at $\lambda \sim 0.93$ μm that may be attributed to a $3p$-$1s$ decay if a new process is introduced which explains the two-photon excitation of a relaxed $3p$ state. This process could be similar to the one proposed for $n=2$ and consist of a mixing of $3s$ and $3p$ states.[4] This assignment is substantiated by the good agreement between the value of the $3p$-$2s'$ energy splitting recently measured[10] by far-infrared spectroscopy, $E_{3p-2s'}=0.102$ eV, and the one given by our experiment ($E_{3p-2s'} \simeq 0.095$ eV).

Additional information on the RES structure is supplied by the direct measurement of the fluorescence decay times τ_p and τ_s, respectively, in experiments (a) and (b) (see Fig. 2 inset). Our results are $\tau_s = 550$ nsec and $\tau_p = 253 \pm 6$ nsec. Our value of τ_s coincides with the well-known result of linear spectroscopy[11] while τ_p is reported for the first time.

We discuss our results on the basis of the FC diagram of Fig. 2. After the selective excitation of the center to the state $|2p\rangle$ (or to $|2s\rangle$), the crystal relaxes with emission of LO phonons. The interaction of the bound electron with the phonon field is recognized to be of crucial importance for the establishment of the RES structure.[12-15] Two kinds of electron-phonon interactions must be considered: the linear interaction of the triplet states $|2p_i\rangle$ with vibrations by the dynamic Jahn-Teller effect and the coupling with the p-mode phonon field (T_{1u} symmetry) which mixes the $2s$ and $2p$ states. These effects may be formalized in a rather complex Hamiltonian which requires a numerical solution of the dynamic problem.[13,15] When the $2s$-$2p$ coupling through the p-mode phonons is strong, the degeneracy of the $2s$ and $2p$ states during the relaxation is removed and a situation of state anticrossing occurs. This effect results in the relaxation of an atom, which is initially prepared in the pure $2p$ (or $2s$) state, to a mixed $2s'$ (or

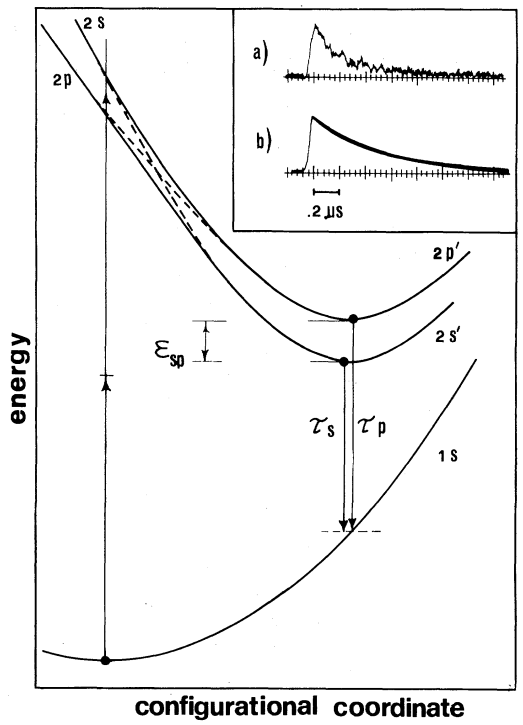

FIG. 2. Franck-Condon diagram of the F center KCl. The two oscilloscope signals at the inset of the figure correspond to the fluorescence decay after two-photon excitation (trace *a*) and one-photon excitation (trace *b*).

$2p'$) state. This process of "dynamic" mixing is obviously an irreversible one and it raises subtle questions about the definition of a state during a rapid crystal relaxation. In general we can say that the anticrossing process will be effective on the population distribution in the RES if the $2s$-$2p$ coupling energy during relaxation is larger than $h\bar{\tau}^{-1}$, $\bar{\tau}$ being the crystal relaxation time. In our case the substantial lack of interference between the two spectra of Fig. 1 shows that the anticrossing process is indeed effective and that the coupling should be strong. Assuming the value of the coupling energy E_g evaluated later in the paper, we obtain $\bar{\tau} > 7 \times 10^{-14}$ sec. It would be interesting to investigate this relaxation process by subpicosecond time-resolution spectroscopy.

The experimental evidence for the anticrossing-mixing process we have just described is of extreme interest in solid-state physics, as we do not know of any other example showing such a clean effect for an electronic process in a solid. In our work we were able to determine for the first time a case in which the adiabatic limit *strictly* holds.

The strength of the vibronic coupling is confirmed by our measurements of τ_s and τ_p. Under the assumption of the phenomenologic Bogan-Fichten model for the RES for crystal distortions in x, y, z directions, $|2s'\rangle = (1+\alpha^2)^{-1/2}(|2s\rangle + \alpha|2p\rangle)$, $|2p'\rangle = (1+\alpha^2)^{-1/2}(|2p\rangle - \alpha|2s\rangle)$, $|2p\rangle \equiv a_1|2p_x\rangle + a_2 \times |2p_y\rangle + a_3|2p_z\rangle$, the radiative lifetimes are given by

$$\tau_s \propto [(1+\alpha^2)/\alpha^2]\,|\langle 1s|\vec{r}|2p\rangle|^{-2};$$

$$\tau_p \propto [1+\alpha^2]\,|\langle 1s|\vec{r}|2p\rangle|^{-2}.$$

The ratio $\tau_p/\tau_s = \alpha^2$ provides direct information on the amount of the s-p mixing. We obtain the large value $\alpha = 0.67$.

Also the value of E_{sp} is relevant for the evaluation of the strength of the electron-phonon coupling. Write the coupling Hamiltonian $H_{el} = G(Q_x\rho_x + Q_y\rho_y + Q_z\rho_z)$ in terms of the phonon and electron operators Q_i and $\rho_i = |2p_i\rangle\langle 2s| + |2s\rangle\langle 2p_i|$. In the case of strong coupling, the coupling energy $E_g = G^2/2\mu\omega^2$ (μ and ω are the lattice effective mass and phonon frequency) may be obtained from the diamagnetic part of the magnetic circular polarization of the luminescence[13]: $\Delta_d(0) \simeq -g_L\mu_B H/E_g$. For KCl it has been found[16] to be $\Delta_d(0)/H = (-9 \pm 1)\times 10^{-8}$. Taking[17] $g_L = 0.95 \pm 0.1$ we obtain $E_g \simeq 60$ meV. Therefore Ham's criterion for the strong-coupling limit, $E_g > \frac{1}{4}|E_{sp}|$, is verified in our case.[13]

In conclusion our work demonstrates in a very direct way that the effect of crystal relaxation on the F-center structure in KCl cannot be accounted for in a satisfactory way by a perturbative approach (Ham and Grevsmühl[14]) but rather by a complete vibronic theory in the strong-coupling limit (Ham[13]; Kayanuma and Toyozawa[15]). Furthermore our work provides the numerical values of the relevant parameters that until now were not available for an exact solution of the dynamic problem.[18]

Thanks are due to Professor L. M. Falicov, Professor Y. R. Shen, Professor G. Chiarotti, Professor N. Bloembergen, Professor M. Aegerter, and Professor T. Iida for enlightening discussions. Also we are indebted to Professor U. Grassano, Professor G. Baldacchini, and Professor R. Cappelletti for substantial help during the preparation of the samples. We appreciate the technical and clerical support of the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory, Berkeley, California.

†Work supported by Gruppo di Ricerca Elettronica Quantistica e Plasmi, Consiglio Nazionale delle Ricerche, Rome, Italy.

*Present address: Physics Department, University of California, Berkeley, Calif. 94720.

[1]A. Gold, in *Quantum Optics*, edited by R. J. Glauber (Academic, New York, 1969).

[2]G. Chiarotti and U. M. Grassano, Nuovo Cimento 46B, 78 (1966).

[3]H. Kühnert, Phys. Status Solidi 21, K171 (1967).

[4]L. Bogan and D. Fichten, Phys. Rev. B 1, 4122 (1970); see also L. F. Stiles, M. P. Fontana, and D. Fichten, Phys. Rev. B 2, 2077 (1970).

[5]R. F. Wood and V. Opik, Phys. Rev. 179, 783 (1969).

[6]W. L. Smith, J. H. Bechel, and N. Bloembergen, to be published.

[7]F. Lüty, in *Halbleiterprobleme*, edited by F. Sauter (Vieweg, Braunschweig, Germany, 1961), Vol. 6, p. 238.

[8]F. De Martini, U. M. Grassano, and F. Simoni, Opt. Commun. 11, 8 (1974), and in *Proceedings of the Eighth International Quantum Electronics Conference, San Francisco, California, 1974—Digest of Technical Papers* (Institute of Electronic and Electrical Engineers, New York, 1974), and in *Proceedings of the International Conference on Color Centers in Ionic Crystals—Extended Abstracts, Sendai, Japan, 1974* (Tohoku Univ., Sendai, Japan, 1974).

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

[10]Y. Kondo and H. Kanzaki, Phys. Rev. Lett. 34, 664 (1975).

[11]L. Bosi, C. Bussolati, and G. Spinolo, Phys. Rev. B 1, 890 (1970).

[12]T. Iida, K. Kurata, and S. Muramatsu, J. Chem. Phys. Solids 33, 1255 (1972).

[13]F. S. Ham. Phys. Rev. B 8, 2926 (1973).

[14]F. S. Ham and U. Grevsmühl, Phys. Rev. B 8, 2945 (1973).

[15]Y. Kayanuma and Y. Toyozawa, in *Proceedings of the International Conference on Color Centers in Ionic Crystals—Extended Abstracts, Sendai, Japan, 1974* (Tohoku Univ., Sendai, Japan, 1974). In that work the effect of the s-mode and d-mode phonons is also considered. The d-mode phonon is found to be of secondary importance while the s mode is found to be effective in causing the red Stark shift and the process of reduction of the orbital g value.

[16]M. P. Fontana, Phys. Rev. B 5, 759 (1972).

[17]J. Margerie, J. Phys. (Paris), Colloq. 28, C4-109 (1967).

[18]The conclusions we have reached in the discussion of our results hold, both qualitatively and quantitatively, in the case of nonvertical alignment of the minima of the RES potential wells of Fig. 2. The only exception is that the energy shift of the spectra of Fig. 1 cannot be entirely attributed to the splitting E_{sp}. The different spectral widths shown in Fig. 1 suggest indeed that the minimum of the $2p'$ vibronic well is slightly displaced toward the left in the diagram of Fig. 2, in agreement with previous indirect measurements of E_{sp}. If we as-

sume the value of E_{sp} reported in Ref. 4, we are able, on the basis of our data of Fig. 1, to draw the exact configuration of the RES structure including the shape and the location of the potential wells in the configurational space. We shall consider thoroughly these important details in a following, more extended paper.

Observation of Higher Sub-band in *n*-Type (100) Si Inversion Layers

D. C. Tsui and G. Kaminsky
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 August 1975)

We have observed population of the heavy-mass sub-band in n-type (100) Si inversion layers at an electron density of $(7.4\pm0.3)\times10^{12}/\mathrm{cm}^2$, corresponding to an energy splitting of 46 meV. These data are inconsistent with results from recent self-consistent-field calculations and confirm that the many-body effects are important.

The n-type inversion layer on a (100) surface of p-type Si has been the subject of many recent studies.[1-7] Although its relatively high electron mobility has led to extensive studies of the electronic properties, especially by using the Shubnikov–de Haas (SdH) effect[1,2] and the cyclotron resonance,[4,5] the energy of its first few quantum levels is still uncertain. Fang and Howard[8] first pointed out that the six conduction ellipsoids are not equivalent in this surface inversion layer. The ground-state energy level, E_0, associated with the two ellipsoids whose long axes are perpendicular to the surface, is lower in energy than E_0', the ground-state energy level associated with the other four ellipsoids. The cyclotron mass characterizing the electronic motion parallel to the surface is $m^*=0.190m_0$ for sub-bands of the two lower-energy ellipsoids and $m^*=0.417m_0$ for sub-bands of the higher-energy ellipsoids. According to their variational calculations, population of the heavy-mass sub-band of E_0' should begin when the electron density (n_s) in the inversion layer exceeds $(3-5)\times10^{12}/\mathrm{cm}^2$. Subsequent self-consistent-field calculations by Stern[6] and by Pals[7] predict that E_0' and E_1 (the first excited-state level of the two lower ellipsoids) are close in energy. At $T=0$ K, E_1 lies below E_0' and population of the E_1 sub-band should begin at $n_s\approx3\times10^{12}/\mathrm{cm}^2$. As SdH and cyclotron-resonance experiments, carried out in this n_s range, have failed to detect the population of any higher sub-bands,[2,5] it becomes suggestive that many-body effects are important in determining these energy level splittings. More recent calculations[9-12] of the exchange and correlation energy of electrons in the E_0 sub-band and its effects on the electron mass and the g factor tend to support this thesis.

In an effort to study quantum effects in Si inversion layers under compressional stresses, we have studied the SdH effect in n-type (100) Si inversion layers at high electron densities (up to $3\times10^{13}/\mathrm{cm}^2$) and have observed the population of a higher sub-band at a threshold electron density $n_{st}=7.4\times10^{12}/\mathrm{cm}^2$. The fact that n_{st} decreases when a compressional stress is applied is evidence that this higher sub-band is the heavy-mass sub-band associated with E_0'. In the rest of this Letter, we shall present these results and discuss their implications for the energy structure and the many-body effects in the inversion layer. Population of higher sub-bands in Si inversion layers on (322), (211), (311), and (811) surfaces has already been reported by Lakhani and Stiles.[13] Kamgar *et al.*[14] have observed optical transitions between the two lowest sub-bands in the accumulation layer on n-type (100) Si. Wheeler and Ralston[15] have reported optical transitions from E_0 to E_2 and several higher sub-bands in photoconductivity measurements.

Our experiments were performed on circular metal-oxide-semiconductor field-effect transistors fabricated on the (100) surface of 25-Ω-cm p-type Si. The gate oxide is thermally grown to 1080 Å thick. The maximum electron mobility of these samples at 4.2 K is ~6000 cm^2/V sec. The SdH effect was studied at 4.2 K, with use of a superconducting magnet capable of fields up to 70 kG. We found that in order to resolve the SdH oscillations at large gate voltage (V_g), where the electron mobility is extremely low, it was necessary to measure the second derivative of the curve of drain current (I_d) versus V_g, i.e., d^2I_d/dV_g^2, by using standard modulation techniques.[16] In this case, we modulate the gate voltage at 500 Hz and measure d^2I/dV_g^2 by detecting the ac com-