[19] M. A. Ivanov, L. B. Kvashnina, and M. A. Krivoglaz, Fiz. Tverd. Tela 7, 2047 (1965) [Sov. Phys. Solid State 7, 1652 (1966)].

[20] T. Gethins, Can. J. Phys. 48, 580 (1970).

[21] H. Bilz, B. Fritz, and D. Strauch, J. Phys. (Paris) Suppl. 27, C2-3 (1966).

[22] E. Hanamura and T. Inui, J. Phys. Soc. Japan 18, 690 (1963).

[23] M. Lax and E. Burstein, Phys. Rev. 97, 39 (1955).

[24] D. A. Ramsay, J. Am. Chem. Soc. 74, 72 (1954).

[25] P. A. Jansson, J. Opt. Soc. Am. 60, 184 (1970).

[26] Ramsay's tables (Ref. 24) pertain to Lorentzian absorption bands and triangular bandpass functions. The convolution of these gives an observed absorption band which is nearly Lorentzian—that is, a function which may be fit by a single Lorentzian either in the main peak or the wings but not both. The measured absorption was of this nature.

[27] P. Vergnat, J. Claudel, A. Hadni, P. Strimer, and F. Vermillard, J. Phys. (Paris) 30, 723 (1969).

[28] R. P. Lowndes, Phys. Rev. B 1, 2754 (1970).

[29] The uncertainty in these positions is roughly 0.02–0.04 cm^{-1} despite the large bandpass. Well-known water-vapor absorption bands near these peaks, observed in our single-beam system, made this accuracy possible.

[30] R. Loudon, Proc. Phys. Soc. (London) 84, 379 (1964).

[31] A. M. Karo and J. R. Hardy, J. Chem. Phys. 48, 3173 (1968).

[32] N. Krishnamurty and T. M. Haridasan, Proc. Phys. Soc. (London) 87, 869 (1966).

[33] J. E. Eldridge, J. Phys. C 3, 1527 (1970).

[34] B. Fritz, J. Gerlach, and V. Gross, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 504.

[35] B. Fritz, J. Chem. Phys. Solids 23, 375 (1962).

[36] D. Bäuerle and B. Fritz, Phys. Status Solidi 29, 639 (1968).

[37] U. Dürr and D. Bäuerle, Z. Physik 233, 94 (1970).

[38] M. deSouza, A. D. Gongora, M. Aegerter, and F. Lüty, Phys. Rev. Letters 25, 1426 (1970).

[39] C. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 104, 599 (1956).

[40] V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. 42, 201 (1970) and references therein.

PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Ultraviolet Absorption Spectra of Photochromic Centers in CaF_2 Crystals

Eugene Loh*
Surface Physics Division, European Space Research and Technology Center,
Noorwijk, Holland
and Department of Materials Engineering and Physical Sciences,
The American University in Cairo, Cairo, Egypt, U.A.R.

(Received 14 December 1970)

Photochromic color centers are known to exist in additively colored CaF_2 doped with La, Ce, Gd, Tb, Lu, or Y. It is also known that these centers consist of one or two electrons bound at the fluorine vacancy adjacent to the trivalent impurity cation. The ultraviolet (uv) absorption spectra of photochromic centers (PC) in CaF_2 were measured from 35 000 to 80 000 cm^{-1}, the band edge of the host crystal, at both room and liquid-nitrogen temperatures. The spectra show two regions of absorption. The low-energy region, up to 57 000 cm^{-1}, has bands at 44 000 and 52 000 cm^{-1}, which are conjectured to be analogous to the L bands of F_A centers in alkali halides. The high-energy region, from 57 000 cm^{-1} on, is characterized by a band at 62 000 cm^{-1}, which is interpreted as charge transfer from PC to nearby impurities. At the band edge, an extra absorption appears in the uv-switched CaF_2: 0.1-at.%-Gd sample, and it is speculated that it is the $4f^7 \rightarrow 4f^6 5d$ transition of Gd^{3+}. This interconfigurational transition is "red shifted" due to the screening effect of electrons, which have been released from the ionized PC and trapped in the vicinity of Gd^{3+}.

I. INTRODUCTION

The photochromic centers (PC) in CaF_2 have aroused much interest[1] in recent years. These centers are produced[2-4] either by x irradiation or by additive coloration of CaF_2 crystals doped with certain rare earths (RE) (La, Ce, Gd, Tb, and Lu) or yttrium. The PC produced by additive coloration can be photoswitched[2-4] reversibly between two states, the thermally stable original state and the ultraviolet (uv)-switched or the ionized state. We shall restrict our discussion to the PC produced by additive coloration[2-4] only.

The absorption spectra of PC below 50 000 cm^{-1} have been extensively studied.[2,3,5] Three absorption bands around 25 000 cm^{-1} have been identified as π, σ, and π transitions from the A_1 ground state.[2,3,5] From the optical[2,3] and EPR studies[6] the PC has been described[3-5] as a complex consisting of a fluorine vacancy with one of the above-mentioned dopants as a nearest neighbor. In the thermally stable state the PC has two electrons and is electrically neutral.[3-5] The uv switching light ionizes[3-5] the PC by releasing one electron, which in

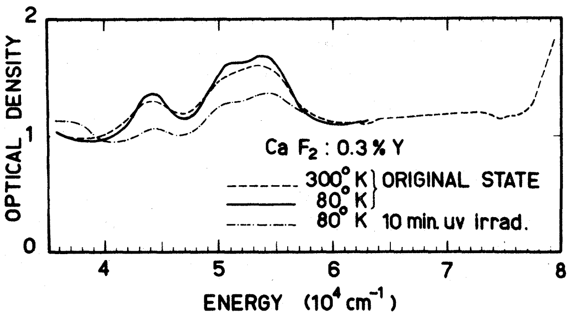

FIG. 1. Ultraviolet absorption spectra of PC in CaF_2: 0.3%Y.

turn reduces an isolated trivalent impurity, i.e., $RE^{3+} + e^- \rightarrow RE^{2+}$. In this work we extend the optical measurements on PC up to the band edge of the host crystal—1250 Å, 10 eV, or 80 000 cm^{-1}—in order to explore new optical transitions of PC in CaF_2 at higher energies. Our results show two regions of absorptions. The first region covers 35 000–57 000 cm^{-1} and has bands at 44 000 and 52 000 cm^{-1}, which are conjectured to be analogous to the L bands of F_A centers in alkali halides. The second region is 57 000–75 000 cm^{-1} and is characterized by charge transfer at 62 000 cm^{-1} from PC to a nearest-neighbor impurity. Finally at the band edge an extra absorption appears in the uv-switched CaF_2: 0.1-at.%-Gd sample and is speculated to be the $4f^7 \rightarrow 4f^6 5d$ transition of Gd^{3+}. This interconfigurational transition is "red shifted" by screening electrons which have been released from the ionized PC.

II. EXPERIMENT

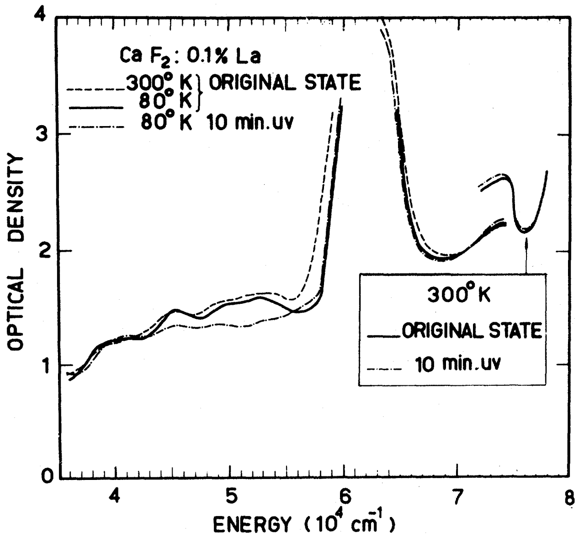

FIG. 2. Ultraviolet absorption spectra of PC in CaF_2: 0.1%La.

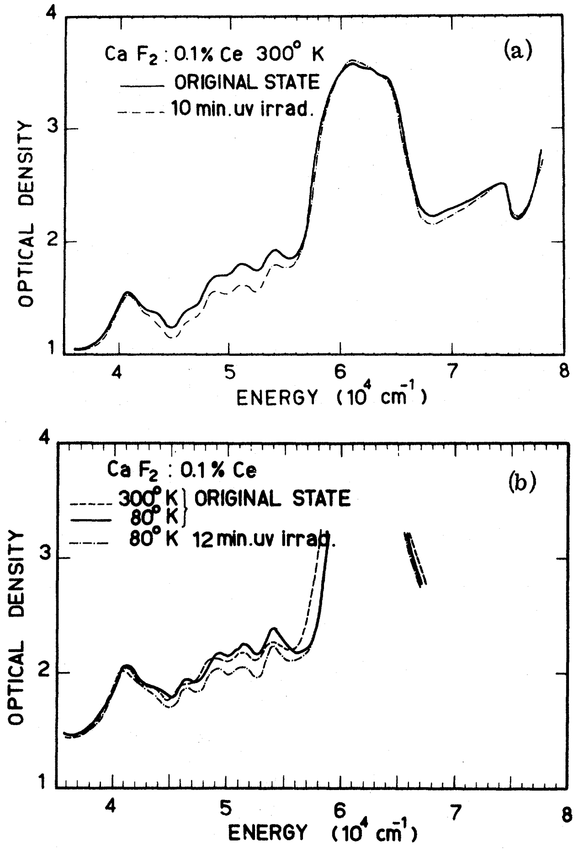

FIG. 3. Ultraviolet absorption spectra of additively colored CaF_2: 0.1%Ce.

Additively colored CaF_2 crystals[2,3] doped with 0.1 at.% of Y and the rare earths La, Ce, Gd, Tb, and Lu, have been generously and promptly supplied by Staebler of RCA Laboratories. All crystals were grown in the RCA Laboratories except CaF_2: 0.1 at.% Lu from Optovac. Optical measurements were made either with samples of McPherson type-218 vacuum monochromator at the exit slit or in a liquid-nitrogen Dewar with a LiF window. A 500-W Hg lamp with 3600-Å transparent uv filter (UG1) served as a source for uv switching. uv irradiation usually lasted about 10 min.

III. RESULTS AND DISCUSSION

The absorption spectra of all PC in CaF_2 are shown in Figs. 1–6. Sample thickness ranges from 0.5 to 1 mm. Figures 3 and 5 also contain $4f^n \rightarrow 4f^{n-1}5d$ bands of Ce^{3+} and Tb^{3+}, respectively, which have been discussed previously.[7,8] Other figures show the PC absorptions only. The discussion of our PC spectra may be divided into three spectral regions: below 57 000 cm^{-1}, between 57 000 and 76 000 cm^{-1}, and above 74 000 cm^{-1}.

In the first region there are absorption bands or pairs of bands at 44 000 and 52 000 cm^{-1}, which are strong in the thermally stable state and consider-

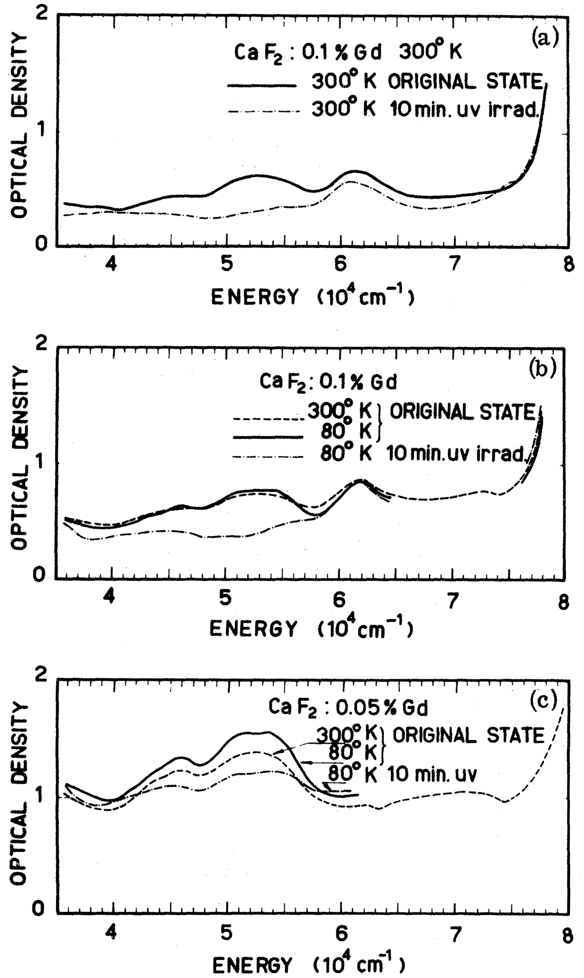

FIG. 4. (a) and (b) Ultraviolet absorption spectra of PC in $CaF_2 : 0.1\%Gd$. (c) Ultraviolet absorption spectra of PC in $CaF_2 : 0.05\%Gd$.

ably weaker in the ionized state. These bands are present in all PC, Figs. 1–5, with the possible exception of Lu-doped CaF_2 in Fig. 6, where the low-energy tail of the huge 62 000-cm^{-1} band may have distorted them. We speculate the bands at 44 000 and 52 000 cm^{-1} to be the analog of the *L* bands of F_A centers[9] in alkali halides. Two observations support this speculation. First, the low-energy, 35 000 cm^{-1}, absorption bands of all PC have been identified[2,3,5] as strong transitions of electrons at the fluorine vacancy adjacent to a trivalent cation. These low-energy bands of PC in CaF_2 are analogous[2,3,5] to the F_A bands in alkali halides. By extending this analogy to the region of higher energy, we therefore speculate that the absorption bands between 35 000 and 57 000 cm^{-1} in Figs. 1–5 are the "*L* bands" of PC in CaF_2, in analogy with the *L* bands[9] of F_A center in alkali halides. Second, it is known[9] that the weak *L* bands of *F* centers in alkali halides can be enhanced by $F \rightarrow F_A$ conversion.

We speculate that the enhancement of the 44 000- and 52 000-cm^{-1} absorption bands from the ionized state (dash-dotted curves in Figs. 1–5) to the thermally stable state (solid curves in these figures) of PC in CaF_2 is analogous to the enhancement of *L*-band absorption in alkali halides by $F \rightarrow F_A$ conversion. The "*L*-band" absorption in PC presumably is more allowed in the thermally stable state than in the ionized state, since the former has two electrons involved in the perturbation of fluorine vacancy by trivalent impurity, while the latter has only one electron.

The present identification is tentative. Further experiments, e.g., photoconductivity of PC samples in this spectral region, are needed to give a more reliable interpretation.

The second region covers 57 000–76 000 cm^{-1}. The absorption in this region is, contrary to that in the first region, insensitive to the photoswitch. A huge band at 62 000 cm^{-1} and a shoulder at 74 500 cm^{-1} appear in the 0.1% La- (Fig. 2), 0.1% Ce- (Fig. 3), and 0.1% Lu- (Fig. 6) doped samples. This 62 000-cm^{-1} band is about one order of magnitude larger than the 44 000- and 52 000-cm^{-1} bands in Figs. 2, 3, and 6. It is also about twice as strong as the well-known 25 000-cm^{-1} band[2,3] of PC in CaF_2. However, the 62 000-cm^{-1} band diminishes successively in the following samples. It reduces approximately to the size of the 44 000- and 52 000-cm^{-1} bands in the 0.1% Gd-doped sample [Figs. 4(a) and 4(b)] and even further in the 0.1% Tb-doped sample [Figs. 5(a) and 5(b)]. Finally it becomes

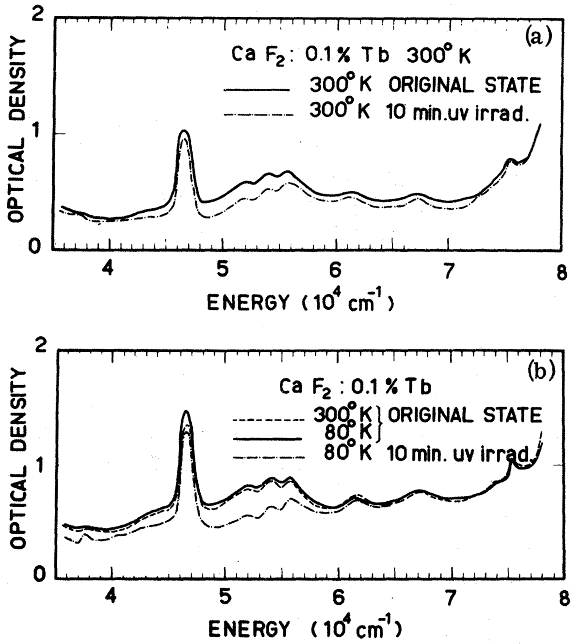

FIG. 5. Ultraviolet absorption spectra of additively colored $CaF_2 : 0.1\%Tb$.

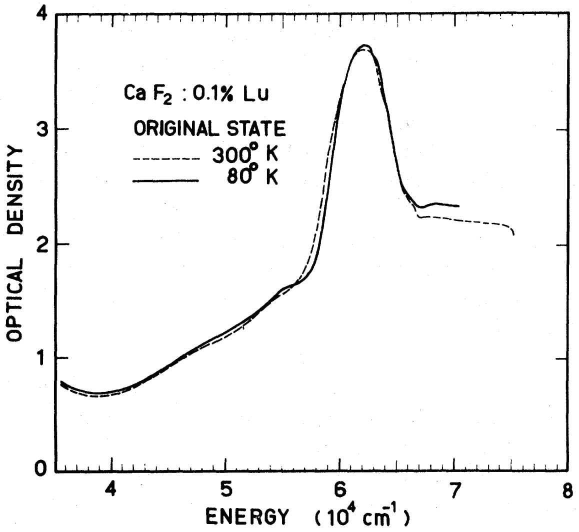

FIG. 6. Ultraviolet absorption spectra of PC in CaF_2: 0.1%Lu.

indiscernible in 0.05% Gd : CaF_2 [Fig. 4(c)] and 0.3% Y : CaF_2 (Fig. 1).

We interpret the 62 000-cm^{-1} band as the charge transfer of an electron from PC to a nearby trivalent impurity, which is of the same chemical species as the one involved in the PC. Three observations support this interpretation: (i) The absorption is strong, (ii) the peak position of the band is independent of the impurity cation, and (iii) the strength of the band depends strongly on the impurity ion and its concentration. Detailed arguments are as follows.

(a) The 62 000-cm^{-1} absorption in Figs. 2, 3, and 6 is reminiscent of the charge-transfer band[10,11] of transition-metal ions (TR) in corundum, whereby the electron is transferred from the anion O^{--} to the 3*d* orbital of TR. Their bandwidths, e.g., 5500 cm^{-1} in Figs. 2 and 6 for 0.1% La and Lu, respectively, and 7500 cm^{-1} in Fig. 3 for 0.1% Ce, are also comparable to the bandwidth[10,11] of charge transfer of TR in Al_2O_3—5600 cm^{-1}. The 62 000-cm^{-1} band is about twice as strong as the well-known 25 000-cm^{-1} band.[2,3] If the oscillator strength of the latter is taken[2] to be 0.3, then that of the former will be 0.6. Because of this large oscillator strength 0.6 we identify the strong 62 000-cm^{-1} band in Figs. 2, 3, and 6 as a charge-transfer band.

(b) The charge-transfer bands of TR in Al_2O_3 have peak positions[10] ranging from 25 000 cm^{-1} for Ni^{3+} to 56 000 cm^{-1} for Cr^{3+} because of varying ionization potential and crystal-field strengths[10] on the various TR. Our 62 000-cm^{-1} band, however, has an approximately fixed peak position for both the lightest rare-earth impurities La in Fig. 2 and Ce in Fig. 3, and the heaviest, Lu, in Fig. 6. This constancy of the 62 000-cm^{-1} peak suggests that the electron transfer is from a PC to a nearby impurity, which is of the same chemical species as the one involved in the PC. This charge-transfer model requires the same transition energy for all dopants,[12] since impurities of the same chemical species, although at different lattice points, are involved both before and after the electron transfer.

(c′) The strength of the 62 000-cm^{-1} absorption decreases progressively in the following order: 0.1%Gd in Figs. 4(a) and 4(b), 0.1%Tb in Figs. 5(a) and 5(b), 0.05%Gd in Fig. 4(c), and 0.3%Y in Fig. 1. We speculate that this strong impurity dependence of the 62 000-cm^{-1} absorption is attributable to the clustering[7,13] of the impurity. Our charge-transfer model requires at least one extra impurity at the nearest neighbor of the PC. Any factor which favors the clustering of ions will therefore enhance the 62 000-cm^{-1} charge transfer. This may explain why the 62 000-cm^{-1} absorption is very strong in the La- and Ce-doped samples while it weakens steadily in the Gd-, Tb-, and Y-doped samples. La and Ce, being the largest ions, tend to cluster around the fluorine vacancy, while the smaller ions, such as Gd, Tb, and Y, may disperse more randomly.

However, it is not clear that the Lu-doped[14] sample exhibits a huge 62 000-cm^{-1} band in Fig. 6 in spite of having the smallest ionic radius among all rare-earth ions. One probable reason is that the Lu-doped sample was grown by Optovac, the others by RCA Laboratories. Presumably the difference in the conditions of crystal growth, annealing, and purity of the materials in the two laboratories will change the distribution of dopants and defects in the crystals.

(c″) For the concentration effect, we expect to have more clusters at higher doping levels. This effect explains our observation that the 62 000-cm^{-1} band in 0.1%Gd : CaF_2 in Figs. 4(a) and 4(b) diminishes to a faint hump in 0.05%Gd^{3+} : CaF_2 in Fig. 4(c).

We do not attempt to interpret the absorption shoulder at 74 000 cm^{-1} in the La-, Ce-, and Lu-doped samples (Figs. 2, 3, and 6, respectively).

The third region is at the band edge of CaF_2. Here we observe a moderate increase in absorption in the uv-switched, or ionized, 0.1% Gd-doped sample at energies > 74 000 cm^{-1} in Fig. 4(b). Samples with other dopants do not exhibit this effect. We speculate that this extra absorption is due to $4f^7 \rightarrow 4f^6 5d$ transitions of Gd^{3+} in a more screened environment. The $4f^7 \rightarrow 4f^6 5d$ transition of Gd^{3+} ($4f^7$) in ordinary CaF_2, being above[15] 80 000 cm^{-1}, is now down shifted because of the screening electrons. These electrons have been released by the uv-switched light and trapped in the vicinity of RE^{3+}. This down shift of the $4f^n \rightarrow 4f^{n-1} 5d$ transition of RE^{3+} in the uv-switched state should also be observed in other photochromic samples. These would be Ce^{3+}- ($4f^1$) or Tb^{3+}- ($4f^8$) doped CaF_2 but not La^{3+}- or Lu^{3+}-doped samples, since La^{3+} ($4f^0$) has no $4f$ electron and Lu^{3+} ($4f^{14}$) has a $4f^{14} \rightarrow 14^{13}$ $5d$ transition even higher[15] than that of isolated Gd^{3+} ($4f^7$), i.e., far beyond the cutoff of CaF_2. We identify the sharp absorptions at 26 400 and 37 800 cm^{-1}, which occur only in the uv-switched photochromic samples[2,3] of 0.1%Ce : CaF_2 and 0.1% Tb : CaF_2, respectively, as the "red-shifted" transitions. They correspond to the transitions of $4f^1 \rightarrow 5d$ at 32 400 cm^{-1} for Ce^{3+} and $4f^8 \rightarrow 4f^7 5d$ at 46 600 cm^{-1} for Tb^{3+}, respectively, in ordinary[15] CaF_2. The amount of the down shift is 6000 cm^{-1} for Ce^{3+} ($4f^1$) and 8800 cm^{-1} for Tb^{3+} ($4f^8$). By interpolation we estimate that the lowest $4f^7 \rightarrow 4f^6 5d$ transition of Gd^{3+} in ordinary CaF_2 would be at 83 000 cm^{-1}, i.e., the sum of $4f^7 \rightarrow 4f^6 5d$ energy of Gd^{3+} in uv-switched CaF_2—74 500 cm^{-1}—and the interpolated down shift of 8400 cm^{-1} for Gd.

We have measured the ultraviolet spectra of nonphotochromic CaF_2 and have confirmed that the spectra presented in this paper are present only in the photochromic CaF_2 crystals.

In conclusion, our ultraviolet spectra of PC in CaF_2 is in general agreement with the present model[2,3,5,6] of vacancy-impurity complex.

ACKNOWLEDGMENTS

The author wishes to thank D. L. Staebler of RCA Laboratories for the generosity of supplying all samples, reprints, and comments; R. C. Alig of RCA for a preprint; B. Fitton and staff at ESTEC for hospitality and frequent assistance; A. Bishay at AUC for support and encouragement; and J. R. Henderson of McDonnell-Douglas Corp. for reading the manuscript.

---

*Present address: The American University in Cairo, Cairo, Egypt, U.A.R.

[1] Z. J. Kiss, Phys. Today 23, No. 1, 42 (1970).

[2] D. L. Staebler, Ph. D. thesis (Princeton University, 1970) (unpublished).

[3] D. L. Staebler and S. E. Schnatterly, Phys. Rev. B 3, 516 (1971).

[4] D. L. Staebler and Z. J. Kiss, Appl. Phys. Letters 14, 93 (1969).

[5] R. C. Alig, Phys. Rev. B 3, 536 (1971).

[6] C. H. Anderson and E. S. Sabisky, Phys. Rev. B 3, 527 (1971).

[7] E. Loh, Phys. Rev. 154, 270 (1967).

[8] E. Loh, Phys. Rev. 175, 533 (1968).

[9] F. Luty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), p. 181.

[10] H. H. Tippins, Phys. Rev. B 1, 126 (1970).

[11] E. Loh, J. Chem. Phys. 44, 1940 (1966).

[12] Among the various rare-earth ions doped in CaF_2, the crystal-field strength on their $5d$ electron varies not more than a few hundred wave numbers [Refs. 7 and 13; E. Loh, Phys. Rev. 184, 348 (1969)]. Therefore, it is not possible from the present uv data to assign the local environment of the rare-earth ions involved in the charge transfer. The bandwidth of the charge transfer, however, may qualitatively indicate the uniformity of the local environment. For example, the bandwidth of 7500 cm^{-1} in Fig. 3 may involve more types of local environment of Ce^{3+} than that of La and Lu in Figs. 2 and 6, respectively, where the bandwidth is 5500 cm^{-1}.

[13] E. Loh, Phys. Rev. 158, 273 (1967).

[14] We also failed to switch this additively colored 0.1%Lu : CaF_2 to the ionized state at liquid-nitrogen temperatures (Refs. 2 and 3).

[15] E. Loh, Phys. Rev. 147, 332 (1966).

PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

LO-Phonon-Assisted Transitions in the Two-Photon Absorption Spectrum of KI†

Richard G. Stafford* and Kwangjai Park
Department of Physics, University of Oregon, Eugene, Oregon 97403

(Received 9 December 1970)

The two-photon absorption spectrum of KI is measured experimentally with high resolution in the exciton region at approximately 6 °K. Fine structure is resolved in which the $2P$ exciton is seen at 6.263 eV and a peak at 6.285 eV is identified as a LO-phonon-assisted transition. The exciton-phonon interaction is calculated using third-order time-dependent perturbation theory. The two-band model is used, where the two intermediate states are virtual excitons excited by the photons and the final state is composed of an exciton and LO-phonon. The theoretical prediction of the strength and location of the phonon-assisted peak agrees favorably with the experiment. Calculations are performed with several values for the hole mass; the value 3.0 is chosen as representing a good average for the fourfold-degenerate hole.

I. INTRODUCTION

Interest in the exciton-phonon interaction in alkali halides has been prevalent for some time. A considerable amount of work has been produced by Toyozawa on the general theory of the line shape