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THE EXCITED STATE-LATTICE INTERACTION
OF THE F-CENTER

28 February 1963

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THE EXCITED STATE-LATTICE INTERACTION
OF THE F-CENTER

by

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ABSTRACT

After an initial discussion of the importance of phonon processes in optical maser research, a brief survey of photon and phonon transitions occurring as a consequence of the optical excitation of the F-center is presented. The existence of metastable excited F-states is postulated to account for a longer than predicted lifetime of the excited F-state. Infrared quenching, photoconductivity and absorption modulation experiments are outlined for the purpose of testing the metastable state hypothesis.

ACKNOWLEDGMENT

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I. INTRODUCTION

Multi-level optical masers were first demonstrated by Maiman using optical pumping in ruby (Ref. 1). A detailed analysis of the levels involved in the spontaneous downward transitions has shown the existence of two sets of doublets separated by $\bar{\nu} = 29 \text{ cm}^{-1}$ in the upper bottleneck (due to the long lifetime of the spontaneous radiative transition with the wave number $\bar{\nu} = 14,000 \text{ cm}^{-1}$ or $\lambda = 6,940 \text{ \AA}$). Furthermore, two sets of doublets separated by $\bar{\nu} = 1 \text{ cm}^{-1}$ are observed close to the ground state (Ref. 2).

The understanding of the pumping transition ($\bar{\nu} = 26,000 \text{ cm}^{-1}$) and the fluorescence transition ($\bar{\nu} = 14,000$) is fairly complete. The opposite is true with respect to the radiationless relaxations designated as 2 - 3, $\bar{\nu} = 29 \text{ cm}^{-1}$ and $\bar{\nu} = 1 \text{ cm}^{-1}$ (Fig. 1) which take place as a consequence of the interaction of the excited electronic states with the lattice. These interactions are of fundamental significance in understanding parameters such as collision-broadened line widths and shapes in solids. On the other hand, the line widths of radiative transitions are an important factor in obtaining a coherent output of an optical maser oscillator operating at a high power level. The simultaneous frequency and amplitude modulation of a ruby optical maser has been measured recently by several investigators (Refs. 3, 4) and was found to be in agreement with the predictions made by the theoretical analyses.

The purpose of the investigation proposed herein is to analyze, both theoretically and experimentally, the details of the transitions which occur in a basic four level optical maser just before the spontaneous radiative downward transition. However, instead of a substitutional Cr^{3+} impurity of the ruby, the study of an electron trapped in a negative ion vacancy is suggested. Because of a much simpler structure, this defect can be treated to a much higher degree of approximation than the complicated paramagnetic ion.

II. THE F-CENTER OPTICAL MASER

Recently, Markham and Mergerian (Refs. 5, 6) proposed a maser scheme in which an electron trapped in a negative ion vacancy is optically excited into a higher state. The electron returns to the ground state through three consecutive transitions, two of which are radiationless while the third emits a photon of about half the pumping energy (Fig. 2). The computed lifetime of the spontaneous radiative

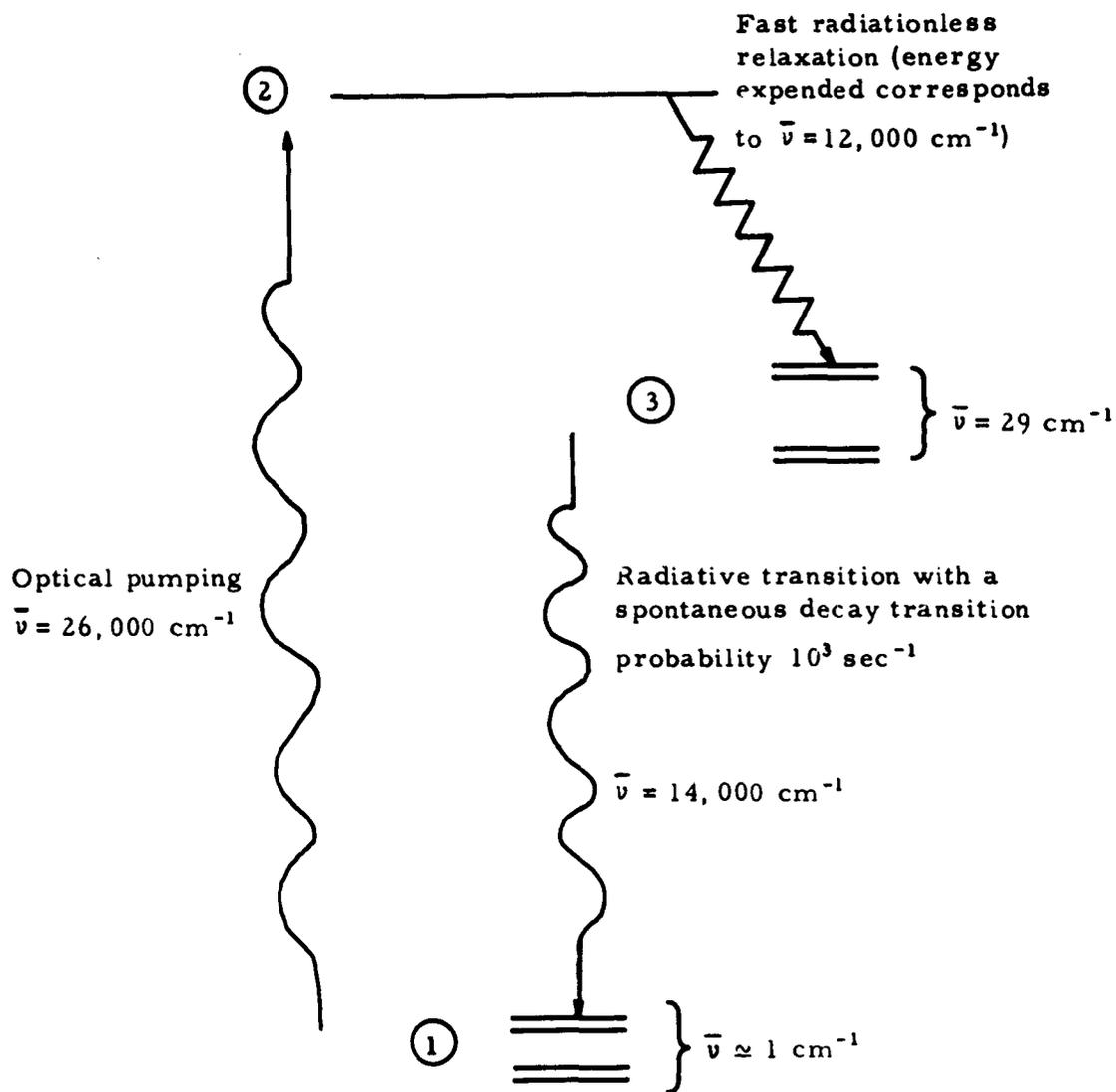
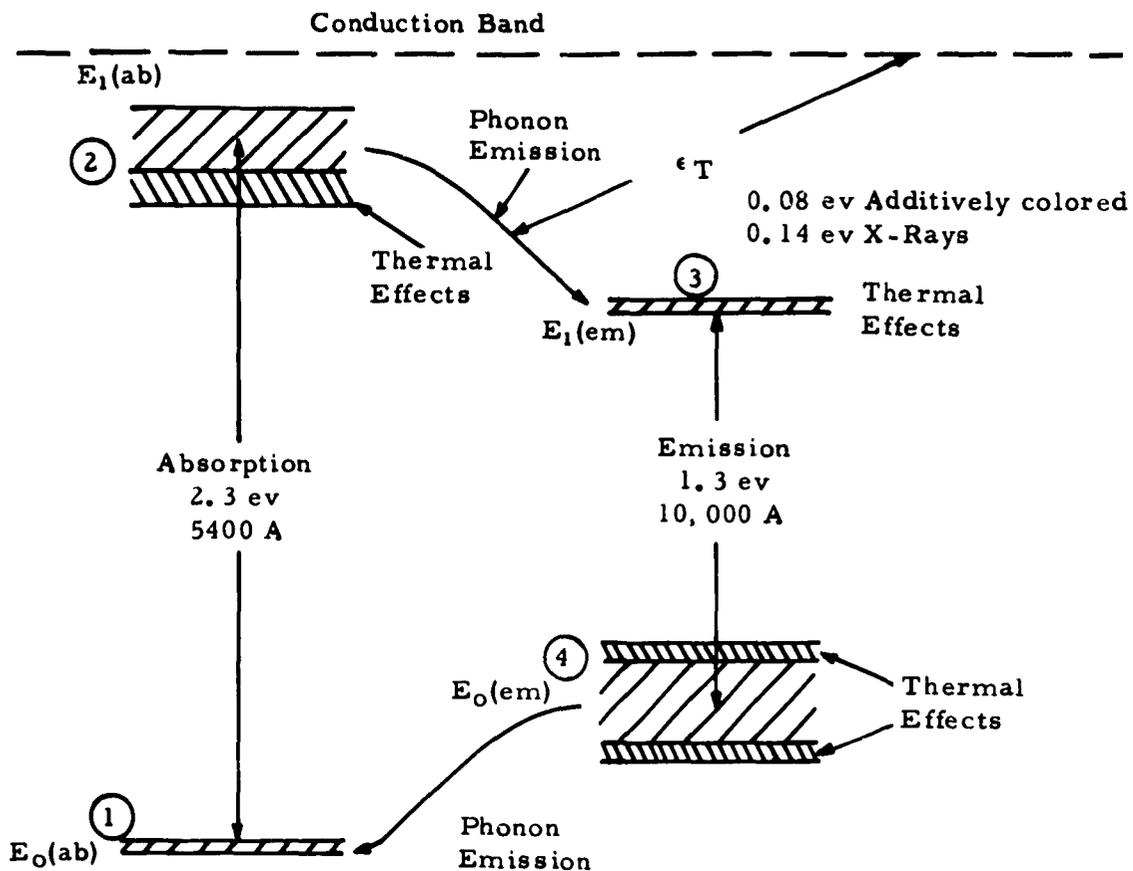


Figure 1. ENERGY LEVEL DIAGRAM OF THE OPTICAL RUBY MASER



Transition 1 - 2 optical pumping by absorption
 $\bar{\nu} = 18,500 \text{ cm}^{-1}$
 3 - 4 radiative downward transition
 $\bar{\nu} = 10,000 \text{ cm}^{-1}$
 2 - 3 and 4 - 1 phonon processes

Figure 2. ENERGY LEVEL DIAGRAM FOR THE F-CENTER IN KCl
 (AFTER MARKHAM)

decay is of the order of 10^{-8} sec. This computation is based on the assumption that the spontaneous radiative decay is adequately described by an electric dipole transition (Ref. 7). The two non-radiative relaxation processes which complete the four-level scheme are assumed to have lifetimes of the order of 10^{-12} sec. each. However, experimental measurements performed by Swank in F. C. Brown's laboratory indicate that for a typical F-center, the cumulative lifetimes for both the first non-radiative relaxation and the radiative transition are of the order of 10^{-6} sec. (Refs. 8, 9). The assumption was made here that a phonon bottleneck does not exist following the radiative downward transition. Since the defects and the processes are relatively simple, the present discrepancy between theory and experiment is rather startling. Two explanations have been advanced thus far to account for this discrepancy:

(1) The radiative downward transition cannot be interpreted in terms of a classical oscillator having the strength of approximately unity (Ref. 10). Smakula used this assumption in deriving the absorption coefficient for the absorption process 1 - 2 (Fig. 2) (Ref. 11).

(2) The relaxation of the excited F-state involves the formation of metastable states which decay through a many-phonon process (Ref. 12). The lifetimes of these metastable states are longer than assumed by Markham for a direct phonon relaxation process 2 - 3 (Fig. 2) (Ref. 7).

The answer to this discrepancy must be found before the F-center excited to ground state transitions can be understood.

III. METASTABLE EXCITED F-STATES

The following approach is proposed to demonstrate the existence of metastable excited F-states and to evaluate their lifetimes.

The first metastable excited F-state in KCl lies energetically 0.08eV and 0.14eV below the conduction band for additively and X-ray colored crystals, respectively. The electron is placed into this state immediately after the adiabatic transition from the ground state which occurs upon the absorption of one 2.1eV pumping photon. The energy level of this metastable state was determined by measuring the activation energy of the thermal ejection of the electron into the conduction band (Refs. 13, 14). The Franck-Condon process of the lattice relaxation follows, during which time the local mode phonons are created. The average energy expended in both local phonon processes

given by transition 2 - 3 and 4 - 1 is greater or equal to the difference between the energy absorbed in the transition 1 - 2 and re-emitted in the transition 3 - 4 (Fig. 2), depending upon the quantum efficiency of fluorescence. At low temperatures, the quantum efficiency of fluorescence is known to be unity. Therefore, about 1eV energy is dissipated in the localized phonon modes during a complete excitation cycle of the F-center. If it is assumed that this energy is equally distributed among both 2 - 3 and 4 - 1 phonon transitions, the lowest metastable excited state is about 0.65eV below the conduction band. On the other hand, the frequencies of the normal phonon modes can be inferred from the Reststrahlen wavelength of the order of 100 microns, corresponding to $h\nu_p \sim 10^{-2}eV$. The existence of the local phonon modes can be ascribed to the fact that a heavy negative ion has been replaced by an electron. This should shift the local phonon mode frequency to a higher value as compared with the normal phonon mode by a factor certainly less than $\sqrt{M_i/m_e} \sim 2 \cdot 10^2$.

The upper value for the energy of a localized phonon, obtained from the above crude estimate, is most likely much too large. This leads to the assumption that the excited F-state-lattice relaxation occurs through a multiphonon process (15) involving the creation of many localized phonons. The energy contained within the localized modes subsequently is dissipated throughout the entire lattice through the coupling between the local and the normal phonon modes. To investigate these assumptions, the following experiments, utilizing the double optical excitation technique, are proposed.

IV. LIFETIMES OF METASTABLE EXCITED F-STATES BY DOUBLE OPTICAL EXCITATION

Three experimental techniques can be suggested to determine the detailed structure of the metastable F-states (the F*-states): (a) the infrared quenching of luminescence, (b) the photoconductivity at low temperatures, (c) the modulation of infrared absorption by the F-center excitation. All three are based on the double optical excitation technique which depends on the following two consecutive optically induced transitions to higher energy states. First, the absorption of a pumping photon of the F-F* energy induces metastable F* states. Subsequently, their excitation by the infrared radiation of a suitable energy below 0.5eV ejects the electron into the conduction band or into a higher metastable state. (To avoid the thermal excitation of the metastable states, the double optical excitation experiments should be performed at temperatures below 100°K).

The ejection of a carrier into the conduction band can be determined by the photoconductivity measurements. At the same time, the luminescence quenching will occur because of the decrease in quantum efficiency. Furthermore, the absorption of an infrared photon in the second excitation process will affect the IR absorption coefficient. Of all these three effects, at least the luminescence quenching has been observed before. In fact, the existence of this quenching delayed the experimental demonstration of luminescence for a number of years (Refs. 16, 17).

V. CONCLUDING REMARKS

The brief discussion presented above did not take into account the existence of the conversion and the aggregate color centers in alkali halides.

In particular, the F' and M centers may cause a spurious infrared absorption which will interfere with the measurements. The F' center (Ref. 18) can be formed at the temperatures of interest in this investigation (e. g., below 100°K) if an F -center in the ground state traps the electron ejected by the second optical excitation from the F^* -state into the conduction band. On the other hand, the M -center concentration will grow if the samples are exposed to light above 100°K (Ref. 19). However, experimental techniques can be designed which will suppress or at least delay the formation of the interfering color centers. These techniques encompass the use of pulsed light sources for either the $F - F^*$ or the $F^* - \text{conduction band}$ excitation. Furthermore, at temperatures below 50°K , the free carriers are scattered predominantly by the ionized impurities instead of the lattice vibrations. Therefore, the mobility of free carriers is high (Ref. 20), and even a weak electric field will suffice to sweep them out. Thus, the formation of F' centers in the optically active region of the sample can be prevented even at low temperatures. The electrical quenching of the F -center luminescence is observed only under high electric fields (Ref. 21), and therefore does not have to be considered at low sweep-out field intensities.

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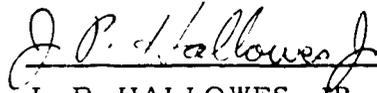
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