

Model for the Electronic Structure of the K and L Bands in Alkali Halides*

ALBERT GOLD

Department of Physics, University of Illinois, Urbana, Illinois

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A speculative model is proposed for the origin of the K and L bands in alkali halide crystals. They are assigned to transitions of the F_2^+ center (an anion vacancy pair plus an electron). This is plausible under the assumption that there is a plentiful supply of anion vacancies in the crystal. It is in general qualitative agreement with experiment. In addition, it possesses an advantage over ascribing these bands to transitions of the F center in that it explains the low quantum efficiency for photoconductivity observed in the L region.

RECENT experimental investigation by Lüty,¹ Inchauspé,² Robe,³ Wild and Brown,⁴ and Brown and Inchauspé⁵ have focused attention on the poorly understood region of the optical absorption spectra of additively colored alkali halides which lies just on the high-energy side of the F band. These workers examined the optical and photoelectric properties associated with the F , K , and L bands and the correlations which exist between them. In an effort to explain his observations, Lüty¹ adopted the view of Mott and Gurney⁶ in identifying the level giving rise to the K band as a higher excited state of the F center, and further ascribed the three L absorptions to still higher states of the F electron. The present note suggests an alternate model for the origin of the K and L bands. This involves an anion vacancy pair and an electron associated with it. It is of a frankly speculative nature, but possesses the virtues of affording an improved explanation of some of the previous observations and of having new properties readily accessible to experimental verification.

In Lüty's interpretation, the K and F bands are taken to belong to well-bound excited states of the F center which lie below the conduction band. The L_1 , L_2 , and L_3 absorptions are then assigned to higher states which overlie the conduction band. Several questions arise which are not immediately answered in this picture. If the L bands correspond to states above the conduction band, a quantum efficiency per absorbed photon of the order of unity is to be expected for photoelectron production. Experimentally, however, this efficiency is found to be about 0.04 in the L_1 and L_2 regions in KCl.⁴ It is thought that the $2p$ (F band) level of the F center lies very close to the bottom of the conduction band.⁷ Thus, it is difficult to understand the origin of a level three or four tenths of an electron volt higher which would account for the position of the K band and still be well bound below the continuum. The "rigidity" of the K band's position and absorption cross-section with respect to temperature changes makes

it improbable that it is caused by the forbidden $1s-2s$ transition.

The L bands are observed as three well-defined peaks whose heights and widths increase rather slowly with energy. The integrated absorption coefficients of a series of "hydrogenic" transitions would be expected to change quite rapidly in the opposite direction. The appearance of a well-defined structure might be attributable to a transition of the F electron to a continuum state which is strongly mixed with another structured set of crystal states such as the excitons. However, this seems rather unlikely in the present instance, considering the transition energies involved. The observance of an Ivey's law⁸ dependence of the peak position on lattice constant in going through the alkali halides characterizes a well localized ("boxed") excited electron and so speaks against the L bands being associated with a spatially diffuse state.

The F_2^+ center [two anion vacancies in (110) coordination, with an electron trapped there] has been discussed theoretically by several authors in connection with the R , M , and N bands.⁹⁻¹¹ Herman *et al.*⁹ have treated it as an H_2^+ molecular ion embedded in a continuous medium characterized by an optical dielectric constant. Gourary and Adrian¹² have discussed this calculation and pointed out its usefulness if one interprets the "dielectric constant" as a phenomenological well-depth parameter to fit F -band data. Nagamiya and Tatsuuma¹⁰ have applied a semicontinuum theory to the problem, and Nagamiya, Kojima, and Kondoh¹¹ have treated this center with a simplified, approximate molecular orbital scheme. These last authors also consider the slight variant with the vacancies in (200) coordination. We shall adopt the viewpoint of Herman, Wallis, and Wallis in discussing the ultraviolet spectra of the aggregate centers. We do this because quick, crude, numerical estimates may be made from available

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¹ F. Lüty, *Z. Physik* **160**, 1 (1960).

² N. Inchauspé, *Phys. Rev.* **106**, 898 (1957).

³ J. Robe, thesis, University of Illinois, 1960 (unpublished).

⁴ R. L. Wild and F. C. Brown, *Phys. Rev.* **121**, 1296 (1961).

⁵ F. C. Brown and N. Inchauspé, *Phys. Rev.* **121**, 1303 (1961).

⁶ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940) p. 114.

⁷ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

⁸ H. F. Ivey, *Phys. Rev.* **72**, 341 (1947).

⁹ R. C. Herman, M. C. Wallis, and R. F. Wallis, *Phys. Rev.* **103**, 87 (1956).

¹⁰ T. Nagamiya and N. Tatsuuma, *J. Phys. Soc. Japan* **9**, 307 (1954).

¹¹ T. Nagamiya, T. Kojima, and H. Kondoh, *J. Phys. Soc. Japan* **9**, 310 (1954).

¹² B. S. Gourary and F. J. Adrian in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 10.

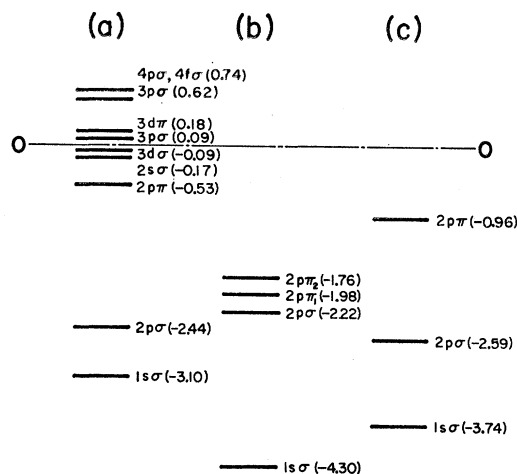


FIG. 1. Some calculated energy-level schemes for the F_2^+ center. (a) From the H_2^+ ion model using a dielectric constant of $k=2.22$ and the tables of reference 11 (the method of Herman, Wallis, and Wallis). (b) Calculated by Nagamiya, Kojima, and Kondoh on a molecular orbital model (the splitting of the $2p\pi$ level has been taken into account). (c) Calculated in the same manner as (b) by Nagamiya, Kojima, and Kondoh, but with the vacancies taken to be in (200) coordination. In KCl the bands of interest have the following peak positions (ev): F :2.3; K :2.71; L_1 :3.6; L_2 :4.3; L_3 :4.95.

data^{13,14} using their method and because picturing these centers as pseudo-diatomic molecules is helpful in orienting one's thinking toward questions of photodissociation and related phenomena. We shall restrict ourselves to specific statements regarding KCl, since the experimental and theoretical work is most extensive for this system. Some calculated energy level schemes for the F_2^+ center in KCl are presented in Fig. 1.

We propose that the K -band absorption is due to a low-lying transition (likely $1s\sigma \rightarrow 2p\pi$) of the F_2^+ center. Considering this configuration as formed from an F center plus an anion vacancy, the law of mass action indicates that the concentration will depend linearly upon F -center concentration, in accordance with Lüty's observation. Simple theoretical considerations place this transition just to the high-energy side of the F band (see Fig. 1 and reference 9) with an oscillator strength of about 0.5. The $2p\pi$ state will be split into two components by the crystal field. It is not unlikely that one of these lies beneath the F band.

The $2p\pi$ state lies well below the "ionization limit" for the F_2^+ and would not be expected to exhibit appreciable photoconductivity. Referring to the configuration coordinate diagram for H_2^+ in a dielectric medium (Fig. 2) as a schematic guide, we see that the $2p\pi$ potential curve has but a very shallow minimum and the possibility of photodissociation exists for the transition. However, this will not necessarily take place, since the energy above the excited F center plus vacancy

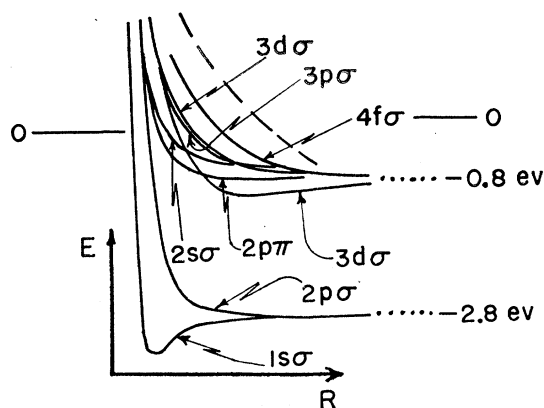


FIG. 2. Configuration coordinate curves for the H_2^+ ion in a dielectric medium ($k=2.22$). The curves have been taken from reference 10, except for the dashed highest state which is inserted merely to indicate that such states may be of importance. The asymptotes represent the energy of an isolated F center in two states.

($H^+ + H$) asymptote to which the excitation takes place may be insufficient to provide for a jump of one of the defects. Also, radiationless transitions may take place to the analog of the metastable $3d\sigma$ state which has a somewhat deeper trough.

In our simple picture one would expect the high energy side of the K band to be determined by the slope of the repulsive part of the $2p\pi$ curve, and thus be insensitive to temperature changes. The peak position would be principally a function of the mean separation of the vacancies determined by the thermal expansion of the lattice, and thus also be quite temperature insensitive. The last two properties are experimentally observed. One would expect K to bleach in F light either via an underlying absorption or through the capture of an electron by F_2^+ (which will have a large cross section due to its charge), converting it to F_2 (an anion divacancy plus two electrons, the analog of H_2). One would expect K to bleach thermally either through thermal dissociation (the ground state of the system has a dissociation energy of the order of a few tenths of an ev), through a vibrational excitation allowing a predissociation to take place through the analog of the $2p\sigma$ state, or via the direct loss of an electron and the consequent formation of two vacancies. A quantitative discussion of the kinetics would require careful consideration of all available mechanisms.

We wish to ascribe the L bands to higher transitions of the F_2^+ center. Since L_1 displays the behavior of a forbidden transition in increasing in integral absorption with rising temperature, it may belong to the $3d\pi$, $3d\sigma$, or (less likely) $2s\sigma$ term. L_2 and L_3 are then taken to belong to higher terms like $3p\sigma$, $4f\sigma$, or others which have an entirely repulsive configuration coordinate. If the excitation to the upper state lies appreciably above the asymptote of its potential diagram, dissociation has a large probability of taking place before the elec-

¹³ R. S. Mulliken, Revs. Modern Phys. 4, 1 (1932).

¹⁴ D. R. Bates, Kathleen Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London 246, 215 (1953).

tron is released into the conduction band even though the term lies above the "ionization continuum" at the point of excitation. Assuming that the slope of the potential curves increase with their energy, the relative widths of the absorptions are expected to increase with energy,¹⁵ as observed. Horizontal transitions may also occur to other states. Such dissociations in the excited state would account for the low quantum efficiency observed in the photocurrent measurements.⁴

A resonant transfer of energy through dipole coupling^{16,17} between F_2^+ and F centers could lead to F -band bleaching under *K* and *L* radiation. F -light irradiation is expected to bleach the L 's via underlying absorptions and F_2 formation as in the case of *K*. It might be noted that the Herman, Wallis, and Wallis model, when used with the data given by Mulliken,¹³ predicts ultraviolet absorption belonging to the F_2 center in the energy region at and just above the *K* band.¹⁸ Thus, Lüty's observation of growth of underlying absorption in the *K*, L_1 , and L_2 region when F and L_3 are bleached is in agreement with the present model.

We also note that F_2^+ is expected to have a very large trapping cross section for electrons. It may be the competing trap for photoelectrons observed in reference 4. F_2 centers thus formed may play a role in the explanation of the infrared photopeaks and associated low-temperature current glow peaks observed in that

work. (Perhaps an electron may be captured into a triplet state of F_2 , preventing the system from falling to the singlet ground state.)

The most obvious new feature of the model proposed is its symmetry. This should be ascertainable in polarized bleaching experiments. However, the situation may be somewhat clouded. We have not explicitly discussed F_2^+ centers having (200) coordination (see Fig. 1 and reference 11). The crude molecular-ion model and the work of Nagamiya, Kojima, and Kondoh suggests that these may have optical properties which do not differ markedly from the (110) configuration. Thus, the symmetry as well as optical properties may be obscured by the presence of divacancies with different crystallographic orientations. Electron spin resonance may be of further assistance in establishing the structure, but the low concentrations and the likelihood of the g value being very near that of the F electron may again make unambiguous interpretation difficult.

We must also admit the possibility that some of the bands in question (say, the *K*) arise from F -center transitions,¹⁹ while the remaining ones belong to F_2^+ . Surely, more detailed study, both experimental and theoretical, is called for.

ACKNOWLEDGMENT

I should like to express my sincere gratitude to Professor F. C. Brown for stimulating and helpful discussions on this subject.

¹⁵ G. Hertzberg, *Molecular Spectra and Molecular Structure*, (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1939) Vol. 1, p. 408 ff.

¹⁶ T. Foerster, *Ann. Phys.* **2**, 55 (1948).

¹⁷ D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).

¹⁸ These are not to be confused with the F_2 center's $^1\Sigma_g^+ \rightarrow 2p\ ^1\Sigma_u^+$ and $^1\Sigma_g^+ \rightarrow 2p\ ^1\Pi_u$ transitions which Herman, Wallis, and Wallis identify as the *R* bands. They may belong to higher electronic states built from $3p$ functions or to $F_2 \rightarrow F_2^+$ -electron transitions.

¹⁹ In a private communication after the preparation of the manuscript, W. D. Compton and B. J. Faraday have informed the author of their recent observations which indicate that the *K* and *F* bands are proportional during their initial growth in KCl and KBr crystals x-irradiated at liquid helium temperature. This evidence suggests that *K* is, indeed, a higher transition of the F center.