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Discovery of F_A(II) centers in KF

L. F. Mollenauer, B. A. Hatch,* and D. H. Olson
Bell Laboratories, Holmdel, New Jersey 07733

H. J. Guggenheim
Bell Laboratories, Murray Hill, New Jersey 07974

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We report the discovery of F_A(II) centers in Na^+-doped and in Li^+-doped KF. Both absorption and emission spectra are given. The formation of the type-II center in KF:Na was unexpected on the basis of simple theory. Also, emission energies are surprisingly close to those of the same center type in KCl and RbCl.

We wish to report here the discovery of two F_A(II) centers[1] in the host KF, the one occurring with a Li^+, the other with a Na^+ doping. (In an F_A center, one of the six metal ions that surround the vacancy is foreign.) Among the various F-like centers that can be created in impurity-doped alkali halides, the type-II centers form a rare but important class that relax to a double-well configuration following optical excitation. (By contrast, the majority, or type-I centers retain the single vacancy.) Until now, the only known cases of F_A(II) behavior were those occurring in the hosts KCl:Li and RbCl:Li[1,2]

This discovery is significant for the following reasons: First, in the case of KF:Na, the observed type-II behavior is forbidden on the basis of the simple ionic-size criterion of Lüty.[1] Although it was already known, through the counter example of RbBr:Li,[2] that satisfaction of that criterion was not always *sufficient* for type-II behavior, until now one might have considered it to be at least a *necessary* condition. Second, the observed luminescence photon energies for both KF centers are remarkably close [~(20–25)% higher] to those of the F_A(II) centers in the chlorides.[1] As will be indicated below, the potential barrier between the two wells of the relaxed configuration is formed at least in part by a halide ion. Since the energy splitting between the ground and exctied states of the relaxed configuration is sensitive to this barrier, our experimental result would seem to indicate that the effective barrier is rather insensitive to the particular halide-ion type. Finally, it has recently been shown that F_A(II) centers can be used to make rather practical tunable cw lasers for the infrared,[3] and the discovery of such centers in KF greatly extends the potential laser tuning range.

The vacancy and double-well configurations of the lattice for F_A(II) centers are shown in Fig. 1; also shown there are the associated energy levels. The vacancy configuration is the normal one, and it applies during the optical-excitation process. But immediately following such excitation, a halide ion moves as shown, forming the double well. (Note that any one of four halide ions adjacent to the foreign ion is potentially capable of making the necessary move.) The system is thus put into its relaxed excited state. The transition to the ground state of the double-well configuration can be made radiatively, and, immediately after, the system relaxes to its normal ground state.

Two distinguishing features of F_A behavior are implicit in Fig. 1. First (in the normal configuration), the presence of the foreign ion causes p_z orbitals to be distinguished from p_x and p_y, such that the absorption exhibits a characteristic twofold splitting. Second, note that there is a 50% probability that the halide ion that separates the two wells of the relaxed configuration will move into the original F_A center vacancy upon return of the system to its normal configuration. When such occurs, the F_A centers axis will have switched orientation by 90°.

In the optically excited type-II center, where the double well is energetically favored over the vacancy configuration, the reorientation described above is completely temperature independent. On the other hand, with F_A(I) centers, an activation energy on the order of 0.1 eV must be supplied in order to achieve such reorientation; hence, the reorientation rapidly freezes out for temperatures $T \lesssim 100^\circ K$. Thus, the experimentally measured temperature dependence of the reorientation process allows type-II behavior to be distinguished from type I in a most unambiguous manner.

The results to be described were obtained in a number of samples. Typically, dopant concentrations (as determined by flame spectral analysis) were on the order of $(0.5-1)\times 10^{-3}$ of the K^+ concentration. In the latest series of experiments,

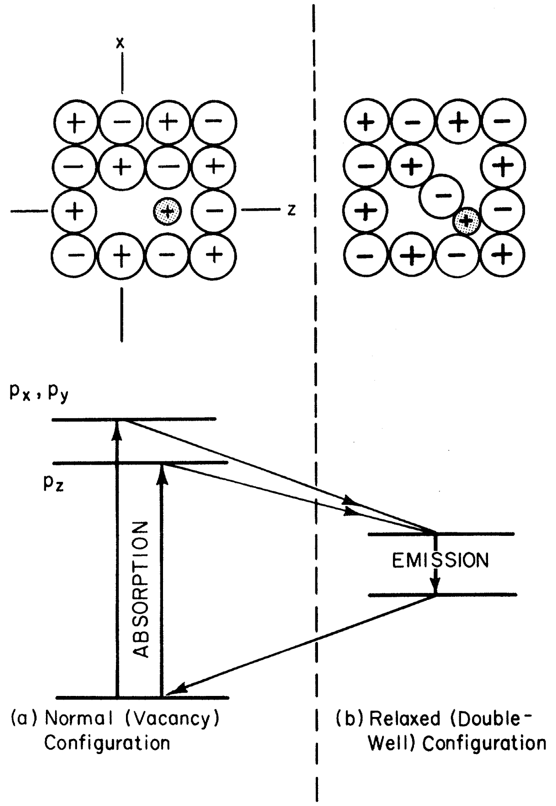

FIG. 1. Above: normal and relaxed configurations of the ions surrounding an F_A(II) center. The small ion is the foreign one (Na$^+$ or Li$^+$). Below: associated energy levels of the F_A(II) center.

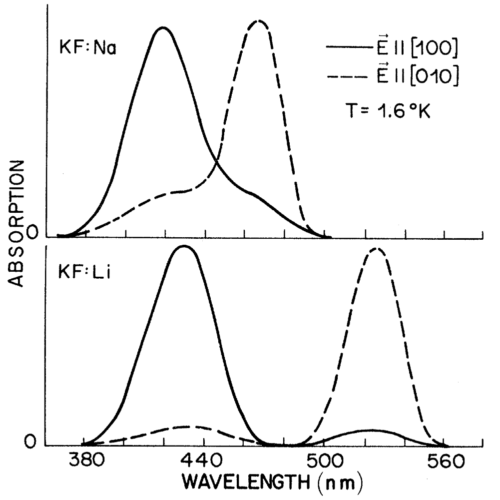

FIG. 2. Dichroic absorption spectra for F_A(II) centers in KF:Na and KF:Li. In both cases, center axes are aligned along [010] (see text).

crystals were prepared from ultra-high-purity KF containing less than 1 ppm of cation impurities, before the Li$^+$ or Na$^+$ dopant was added; in this way, identification of each spectrum with a particular dopant was made absolutely certain. Some samples were colored additively, while others were colored by exposure to x rays. Conversion[4] of F to F_A centers was carried out by exposing the sample to F-band light for 30 min at −40°C.

The absorption spectra of the F_A centers in KF are shown in Fig. 2, for fully aligned systems. Alignment was achieved by pumping the higher energy band with light polarized along [100] and propagating along on [001] axis. The dichroic spectra were then obtained by looking along [001] with light polarized in both [100] and [010] directions. For KF:Li, the absorption peaks occurred at $\lambda = 429$ nm (2.89 eV) and $\lambda = 525$ nm (2.34 eV); for KF:Na, the corresponding figures were $\lambda = 419$ nm (2.96 eV) and $\lambda = 467$ nm (2.65 eV). The 0.55-eV peak separation in KF:Li represents by far the largest splitting seen to date in F_A centers.

By changing the pump polarization from [100] to [010], the center alignment axis could be switched from [010] to [100], as indicated by the corresponding change in the dichroic spectra. This switching was obtained just as completely at $T = 1.6$°K as at 77°K.[5] Similar reorientation effects, also consistent with the model, could be obtained by pumping the lower energy absorption band. Thus there is no doubt that both centers exhibit type-II behavior.

The emission spectra of the F_A(II) centers in KF at 77°K are shown in Fig. 3. The curves shown have been corrected for grating and detector response. For KF:Li, the band peaks at 553 meV ($\lambda = 2.24$ μm) with a width at the half-

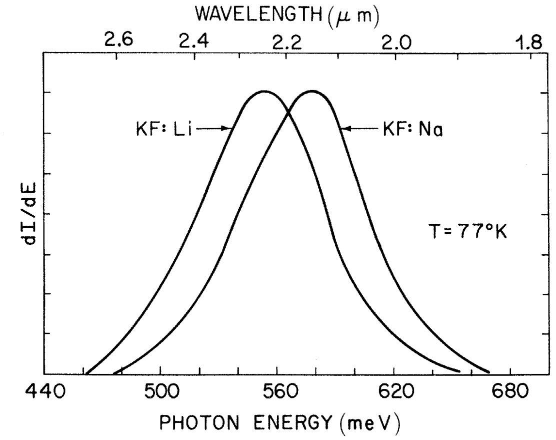

FIG. 3. Emission spectra of F_A(II) centers in KF:Na and KF:Li. The spectral density dI/dE is proportional to emitted photons per unit time per unit energy.

power points of 76 meV; for KF:Na, the band peaks at 578 meV ($\lambda = 2.15\ \mu$m), with essentially the same half-width. For comparison, the F_A(II) emissions in KCl:Li and RbCl:Li peak at 460 and 430 meV, respectively.

Selective excitation experiments carried out with various lines of an argon-ion laser on an optically thin sample correlate the emission spectra of Fig. 3 very well with that part of the absorption spectra of Fig. 2 that could be covered. Also, the expected dependence of the emission intensity on pump polarization (with respect to the crystal axis) was obtained

It would be most useful to have a theory that could correctly predict the type-II or type-I behavior of a given system. Ong and Vail[6] have attempted such a calculation for the systems KCl:Li (type II) and KCl:Na (type I) with mixed success. Perhaps with two more examples of type-II behavior as a guide, the major sources of error in such treatments could be uncovered, and more satisfactory results obtained.

It would be equally useful to have a satisfactory way of predicting F_A(II) emission energies. A closely analogous system, the F_2^+, has been treated with remarkable success as an H_2^+ molecular ion.[7] Perhaps it is not unreasonable to expect a similar, essentially point ion, model to work for the F_A(II) center. Until now, however, known F_A(II) behavior was too rare to allow for meaningful test of any such model against experiment.

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*Present address: Westinghouse Bettis Atomic Power Div., West Mifflin, Pa.

[1] For a good general description of F_A centers, see F. Lüty, in *The Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), Chap. III.

[2] H. Ohkura, Prog. Theor. Phys. Suppl. 46, 11 (1970).

[3] L. F. Mollenauer and D. H. Olson, Appl. Phys. Lett. 24, 386 (1974).

[4] H. Härtel and F. Lüty, Z. Phys. 177, 369 (1964).

[5] The reader should be advised that we made no attempt to measure the relative quantum efficiency of the reorientation process; in this sense the result quoted here is purely qualitative in nature. However, Irwin Schneider and Wm. C. Collins of the Naval Research Laboratory (Washington, D. C.) have recently discovered a considerable decrease in quantum efficiency of the reorientation with decreasing temperature below 77 °K, for the case of KF:Na. Their result may well indicate that the energetic difference between type-I and type-II relaxed excited states is extremely small in the case of the KF:Na F_A center. Many thanks to Schneider and Collins for permission to quote their unpublished result here.

[6] C. K. Ong and J. M. Vail, Phys. Rev. B 8, 1636 (1973).

[7] M. A. Aegerter and F. Lüty, Phys. Status Solidi B 43, 245 (1971).