tude is about 1000 times that predicted by the usual theory of ionic conduction; it has the same sign and approximately the same temperature dependence. There is a relatively slight dependence upon the amount of impurity and the type of alkali halide. The dependence of the nonlinearity upon temperature, voltage, and specimen thickness, and its independence of electrode material or preparation, favor the viewpoint that it is a bulk property of the material rather than ascribable to electrode effects of polarization. On the other hand, there is a frequency dependence, which favors the opposite viewpoint, as does the observation that gross deterioration of the electrodes increases the nonlinearity.

Several mechanisms for the effect are discussed. But none, at present, seem to offer much hope of an explanation.

New Data on the Relaxed Excited State of the F Center*

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Ionization energies ΔE and lifetimes τ_R of the excited state of the F center have been measured in various alkali halides. The experimental values of ΔE have been plotted versus $(m^*/m)(1/\epsilon_S^2)$, following Fowler's idea that in emission the excited-state wave function is very broad. The hydrogenic model seems to fit the data very well, and Fowler's theory finds strong experimental support.

INTRODUCTION

THE lifetime of the excited state of the F center has recently been measured, and the results are of fundamental interest.[1] Subsequent data on the lifetime of the excited F_A center[2] and a theoretical discussion by Fowler[3] have led to the hypothesis that the excited-state $2p$ wave function, after relaxation of the lattice, is not confined to the vacancy, as the ground state is, but is considerably spread out in the surrounding lattice.

The position in energy of the F band in the different alkali halides fits the well-known Ivey law.[4] Here one is dealing with the F center in absorption, and the lattice parameter determines the energy position of the band. On the other hand, it has been proposed[3] that an effective dielectric constant is the important factor in the case of emission. For NaCl this effective dielectric constant turns out to be about 75% of the static value ϵ_S. By using such a value it is possible to correctly estimate[3] the wavelength of emission, the ionization energy of the excited state ΔE, and the radiative lifetime τ_R.

In order to confirm the theory of Fowler[3] an effort has been undertaken in two directions: first, the electric field ionization of the excited F center has been investigated and interpreted along the general lines of Euwema and Smoluchowski.[5] These results will be reported elsewhere.[6] Second, the values of ΔE and τ_R for the excited state have been measured in different alkali crystals. A relation has been sought between the observed values of ΔE or of τ_R and the known dielectric constants ϵ_S.[7] The results will be reported in this paper and our attention will be directed mainly to the ionization energy.

EXPERIMENTAL DETAILS

The apparatus that we used to observe luminescence and photoconductivity consisted of the high intensity, short duration, light source developed by Swank[1] plus an RCA 7102 photomultiplier, a fast amplifier, and oscilloscope. The measurement technique has been described elsewhere.[1,2] For RbCl it was possible to measure both luminescence and photoconductivity, but for RbBr and CsBr only the photoconductivity yield and lifetime were measured, since their emission is out of the range of the available photomultipliers.[8]

For the RbCl measurement we used both hydrided and additively colored crystals, but for RbBr the experiments were performed only on hydrided specimens and for CsBr only on x-rayed material. In every case

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[5] R. N. Euwema and R. Smoluchowski, Phys. Rev. 133, A1724 (1964).

[6] G. Spinolo and W. Beall Fowler (to be published).

[7] F. C. Brown in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, London, 1962), p. 325.

[8] An attempt was made to measure photoconductivity lifetimes in the range 4.2–200°K in LiF, but this was unsuccessful. The crystals were probably very impure, so that trapping and also non-radiative decay processes may be important. W. D. Compton and S. Schnatterly (private communication) did not find luminescence in LiF at 4.2°K. These facts are very puzzling and worthy of further investigation.
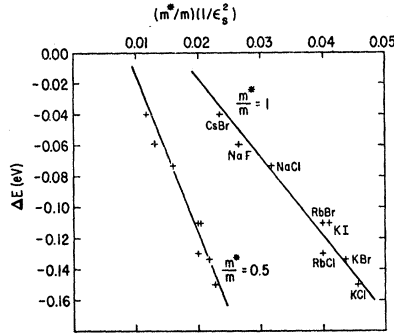
FIG. 1. Ionization energies ΔE for the excited relaxed state of the F center, plotted as a function of $(m^*/m)(1/\epsilon_S{}^2)$ according to Eq. (3).

TABLE I. Radiative lifetime τ_R, depth of the excited state below the conduction band ΔE, frequency factor $1/\tau_0$ for the F center; static dielectric constant ϵ_S (at room temperature), exciton reduced mass μ for the corresponding alkali halides.

Material	τ_R (μsec)	ΔE (eV)	$1/\tau_0$ (10^{12} sec^{-1})	ϵ_S	μ
NaF[a]		0.06		6.0	
NaCl[b]	1.00	0.074	0.12[d]	5.62	0.31
KCl[b]	0.57	0.150[c]	4.03	4.68	0.36
KBr[b]	1.11	0.135	14.00[d]	4.78	0.47
KJ[b]	2.22	0.11	3.50[d]	4.94	
RbCl	0.60	0.13[c]	1.75[d]	5.0	0.36
RbBr	0.84	0.11[d]	0.67[d]	5.0	
CsBr	1.54	0.04[c]	0.12[d]	6.51	

[a] Unpublished data from Podini (Istituto di Fisica, Università di Milano).
[b] From Refs. 1 and 2.
[c] Averages from quantum yield and lifetime data.
[d] From photoconductivity lifetime data.

the concentration of F centers was around 10^{16}cm^{-3}. The absorption bands were measured before and after the luminescence and photoconductivity measurements.

ANALYSIS OF THE DATA AND DISCUSSION

The data on lifetime τ, observed as a function of temperature, were analyzed[1,2,9] according to

$$1/\tau = (1/\tau_R) + (1/\tau_0)e^{-\Delta E/kT}, \qquad (1)$$

where τ_R is the radiative lifetime and $1/\tau_0$ is a frequency factor. Values of τ_R, ΔE, and $1/\tau_0$ can be determined by fitting Eq. (1) to the data. The values of ΔE can also be obtained by observing the yield or efficiency η_i as a function of temperature. In this case one plots

$$(1/\eta_i) - 1 = (\tau_R/\tau_0)e^{\Delta E/kT}. \qquad (2)$$

It has been pointed out[2,5] that Eqs. (1) and (2) represent only a first approximation since a slow rise in lifetime is usually observed at very low temperatures. So far an explanation has not been found for this phenomenon.

Since the excited wave function is very spread out in the lattice[3] we analyze the observed values of ΔE in terms of a simple hydrogen atom model for a dielectric continuum. The excited state of the F center is thought to correspond to the $n=2$ energy level. The depth of this level below the continuum is therefore given by

$$\Delta E = -(e^4/2\hbar^2(2)^2)m^*/\epsilon_S{}^2. \qquad (3)$$

Now, if this formula applies at all, the ΔE is an optical depth, whereas the measurements give a thermal depth. These may not be too different and, in any case, they are usually related by a constant factor. Low temperature values of ϵ_S are not available in all cases so we use the room temperature values. The variations from room

to low temperature are not great, probably of the order or less than 10% in all cases. The results for ΔE are plotted according to Eq. (1) in Fig. 1. Two values of m^*/m are used. The lighter mass $m^*/m = 0.5$ may be somewhat better since it is only slightly larger than the values of reduced mass μ estimated from exciton binding energies[10,11] and listed in the last column of Table I.

It can be seen from Fig. 1 that the various alkali halides can be ordered according to their dielectric constants. This is probably the main virtue of such a plot. Since the straight lines in Fig. 1 do not pass through the origin as Eq. (3) predicts, it may be that the effective masses change somewhat in going from KCl to CsBr. It is probably not worth speculating further until better values of ϵ_S, m^*, and the optical energy ΔE become available. We do think, however, that the data presented here give support to Fowler's theory.[3] They also allow for the possibility of predicting values of ΔE for other alkali halides and may stimulate research directed toward more exact determination of the relevant parameters.

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