ential angular cross sections from single crystals represent an additional and independent check of a lattice dynamical model.

The method is not as sensitive to the details of the model as a double differential cross section measurement; however, it can be employed advantageously when large single crystals or very intense neutron sources are not available.

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Photochemical Conversion of F Centers to M Centers in KCl, KBr, and CsBr*

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The mechanism for the formation of M centers from F centers upon irradiation in the F band is discussed. The evidence favoring F_2^+ (or M^+) centers as intermediate states is shown to be less convincing than formerly believed. Measurements of the activation energy of the reaction rate have been made for F-to-M photoconversion in additively colored KCl (0.35 eV), KBr (0.39 eV), and CsBr ($\sim$0.1 eV). The "activation vloumes" for F-to-M conversion in KCl and CsBr have been measured. They are much smaller than those estimated for free anion diffusion. The same mechanism for F-to-M conversion seems to obtain in these three salts.

INTRODUCTION

When an alkali halide containing F centers is irradiated at an appropriate temperature with light in the F band, M centers may form according to the reaction $F+F\rightarrow M$. The reaction rate varies with temperature as $\exp(-E/kT)$ over the small range of temperature in which it can be measured. The remarkable feature of the reaction rate is that E, the "activation energy," is very small, being about 0.4 eV in KCl. Since the M center is known to consist of two electrons trapped at two anion vacancies in nearest-like-neighbor positions,[1,2] it is clear that when M centers are formed from F centers, entities containing anion vacancies must migrate. The activation energies measured for other vacancy-migration processes in KCl are much larger than 0.4 eV. An anion vacancy diffuses with an activation energy[3] of 0.95 eV, while F centers diffuse with an activation energy[4] of 0.94 eV.

The mechanism by which two F centers combine to form an M center is of considerable interest. Two processes have been proposed. The F-band irradiation first ionizes some F centers, resulting in a crystal containing anion vacancies (α centers), F centers, and F' centers which formed upon the capture of electrons by some of the original F centers. The F' centers are metastable. Van Doorn[5] proposed that the α centers are attracted to F' centers, producing M centers directly. An alternative process[6] is one in which α centers are attracted to F centers, producing M^+ centers (F_2^+ centers[7]) which subsequently capture electrons to become M centers. Although we have implied above that α centers move, in both models the other defect, F or F' center, could move toward the α center. (Crawford[8] has proposed that F' centers may move.) In any case, the low activation energy of the reaction rate constant for photochemical F-to-M conversion remains a puzzle.

Asai and Okuda[9] conducted the most thorough experimental study of the reaction rate constant for optical F-to-M conversion in KCl. They considered the optical ionization of F centers, the capture of electrons by α centers and F centers, and the thermal ionization of F' centers. By comparing the dependence of the reaction rate on temperature, F-center concentration, and F-light intensity with that expected for the two mechanisms discussed above, they concluded that the "M^+ process" ($\alpha+F\rightarrow M^+$, then $M^++e^-\rightarrow M$) occurs, rather than the "direct process" ($\alpha+F'\rightarrow M$). The small activation energy then arises because E is the activation energy for anion vacancy diffusion minus

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one-half the thermal ionization energy of the F' center. The thermal ionization energy of the F' centers enters the picture because it affects the concentration of α centers.

Recent experiments on LiF have shown that there is a transient M^+ band during F-to-M conversion, strongly suggesting an M center-formation mechanism involving M^+ centers.[10–12] Subsequently, Farge *et al.*[13] proposed that M^+ centers were the intermediate states in F-to-M conversion in LiF, and perhaps in other alkali halides[14,15], and that the electron on the F center tended to form a covalent bond between the two anion vacancies (one in the F center, the other the α center) when they are separated by several interionic distances. This covalent binding tends to lower the energy for motion of the free anion vacancy toward the value observed in F-to-M conversion. Although this model does not give a simple $\exp(-E/kT)$ form for the reaction rate, it may effectively do so if the temperature range of the experiments is sufficiently restricted. Farge *et al.* presented other arguments which make the M^+ mechanism seem likely for optical conversion in LiF.

We have tried to measure the activation energy for F-to-M photoconversion in several alkali halides, primarily to determine whether a low activation energy occurs in other alkali halides, or only in KCl and LiF. Activation energies were obtained for KBr and CsBr. We also measured the activation volume for F-to-M photoconversion in KCl and have estimated this quantity for CsBr.

Another purpose of the present paper is to point out that it may be possible to interpret the work of Asai and Okuda,[9] and of Farge *et al.*[13] (for salts other than LiF) on the basis of the direct mechanism instead of the M^+ mechanism. We do not favor the direct mechanism but merely wish to point out that a clear choice between the two mechanisms cannot be made yet.

COMMENTS ON MODELS PROPOSED

Asai and Okuda[9] show that both models predict a reaction rate proportional to the square of the F-center concentration. They measured the dependence to be as the 1.34th power and attribute the difference to an inhomogeneous distribution of those F centers that become M centers. They observed the reaction rate to vary as the 0.65th power of the intensity of irradiation in the F band. Others have found the first power[5] and 0.27th power.[6] They predict the 0.5th power if M^+ centers are formed as an intermediate, and the first power if M centers form directly. Hence their data favor the M^+ mechanism. The activation energy E is the anion-vacancy diffusion-activation energy minus either the thermal ionization energy of the F' center (direct formation of M centers) or minus one-half this (M^+ mechanism). For the value of the anion-vacancy activation energy in KCl, they chose 0.6 eV, measured by Härtel and Lüty for $F\rightarrow F_A$[16] and $F\rightarrow Z_1$[17] conversion. This gave $E=0.35$ eV for the M^+ mechanism and 0.1 eV for the direct formation of M centers, to be compared with the observed 0.4 eV. However, if one uses Fuller's[3] value for the activation energy of anion migration, one gets 0.7 and 0.45 eV, respectively, with the value for the direct mechanism in better agreement with experiment. We believe that may not be consistent to use Härtel and Lüty's value in this analysisbe cause it may already include corrections similar to the thermal ionization energy of the F' center, or one-half of it, and is thus probably a composite energy, just as E is, on the basis of the work of Asai and Okuda. Moreover no covalency was considered. If any covalent bonding occurs in the M^+ mechanism, the experimental value of E should not agree with that calculated on the above model, but it should be smaller. The possibility that the F or F' center moves instead of the α can be tested only when F and F' activation energies for motion are available.

The covalency effect suggested by Farge *et al.*[13] is very appealing, but we suggest that it *may* also apply to the attraction between α centers and F' centers. There is a long-range Coulomb force between these two defects, but it does not lower the activation energy for the jump of either defect very much because it does not depend rapidly enough on distance. There are no good estimates of the "size" of F' centers. Calculations have been carried out[18] using a semicontinuum model similar to that used on F centers.[19] They indicate that the F' center is about as compact as the F center, an effect of polarization, both centers being described by potentials that were evaluated in a similar fashion. Thus as an α center and an F'-center approach, the F' center polarizes. When the F'-center wave function begins to overlap the α center, some covalent bonding occurs. Then symmetry dictates that both defects resemble polarized F centers. The calculation of the binding of an α center to an F center was done[13] by inserting a dielectric constant in the Coulomb potential for an H_2^+ molecule-ion. The over-all similarity of the ground-state

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[14] Y. Farge (private communication) has pointed out that Rabin (Ref. 15) observed a transient absorption band at 1.35μ in KCl that had been x-rayed at 78°K, then warmed in the dark. This band was strongest at 248°K. When the crystal reached 300°K, the M band was much larger than at 78°K. This band is probably the F_2^+ band, identified later by Schneider and Rabin (Ref. 7). Thus M^+ centers appear to have been observed during F-to-M conversion in KCl under appropriate conditions. Such a band would be difficult to separate from the F' band in experiments in which M centers are made from F centers by irradiating in the F band.

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configuration-coordinate curves of H_2^+ and H_2 at larger internuclear separations[20] makes it likely that an analogous treatment carried out for the H_2 molecule would yield some covalent binding between an α center and an F' center. The covalent binding of these two molecules is different, but the lowering of the activation energies for the jump of a defect is proportional to dV/dr, not V, the binding energy. (The usual configuration-coordinate curve for H_2 is for dissociation into two neutral hydrogen atoms, rather than the charged H^+ and H^-, the latter being similar to the α and F' centers. The covalent contributions to both types of configuration coordinate curves for H_2 should be comparable, however.) In short, a covalent contribution to the activation energy for F-to-M conversion by the direct mechanism may be expected. We therefore suggest that there is need for a more detailed theoretical investigation of "M" and "M^+" centers with large intervacancy separation, taking into account polarization in both models.

EXPERIMENTAL RESULTS

Additively colored blocks of crystal were cleaved or cut into several samples of similar thickness. The rate of formation of M centers was measured on a Cary 14R spectrophotometer at several temperatures, using a freshly quenched crystal for each temperature. The F band was bleached with F light at fixed temperature. After various time intervals the height of the M band was measured. The M band grew linearly with the time of irradiation in the F band, then saturated, then diminished as R bands formed. As a measure of the reaction rate, we took the maximum slope of the curve of M-band peak absorption coefficient versus time of irradiation in the F band, using a constant photon flux. See Fig. 1, although there, pressure, rather than temperature, is the parameter varied between runs. The data were normalized to constant initial F-center concentration by assuming the rate to have been linear in this quantity. Since the initial F-center concentrations varied by only about 20% among samples of any one salt, the correctness of this assumption is not critical. The plots of the logarithm of the rate versus inverse temperature were straight lines whose slope gave E, the activation energy. Our value of 0.35 eV for KCl (for an F-center concentration of 5.8×10^{16} cm^{-3}) is in good agreement with the work of several others,[9,21–23] but higher values have been found by other workers.[5,6,24]

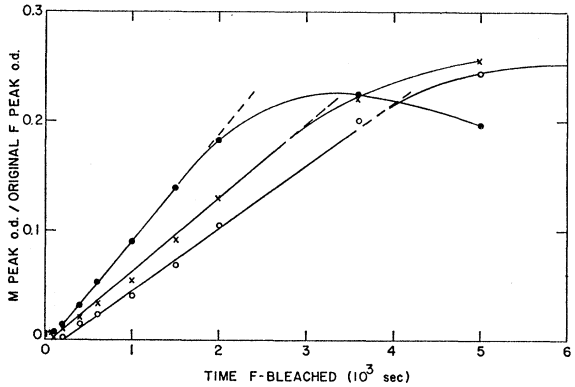

FIG. 1. M center concentration (o.d. = optical density) versus time of irradiation in the F band at constant photon flux. The M-center concentration is proportional to the optical density at the M-band peak. The curves are normalized to constant initial F-center concentration. All data were taken at 24.0°C. ● = 0.001 kbar; × = 2.065 kbar; ○ = 4.170 kbar.

Table I[25–30] lists the values of E for KCl, KBr, and CsBr. The value for CsBr is very rough. Three series of runs were made on three different CsBr crystals. The values of E obtained were 0.10, 0.07, and 0.07 eV. Several other CsBr crystals yielded too few M centers for convenient study, despite reasonable F-center concentrations, while another crystal yielded $E=-0.07$ eV. Clearly another competing reaction was occurring in the last crystal, and the extent of its occurrence in the first three crystals is not known. Attempts to obtain E in NaCl and RbCl were not successful. The low values of E in KBr and CsBr suggest that the mechanism for F-to-M photoconversion is the same in these salts and in KCl.

TABLE I. Activation energies (eV).

Initial F-center concentration (10^{16} cm^{-3})	KCl 5.8	KBr 15	CsBr 10–20
F-to-M conversion	0.35	0.39	0.1
Anion vacancy motion	0.95[c] 1.04[d]	0.87[e] 1.02[f]	0.27[g]
F' thermal ionization	0.54[h] 0.62[i]	0.35[h]	
Calculated[a] for F to M^+	0.64–0.77	0.70–0.85	
Calculated[b] for direct F to M	0.33–0.50	0.52–0.67	

[a] Using expressions of Ref. 9—second row of above table minus one-half of third row.
[b] Using expressions of Ref. 9—second row of above table minus third row.
[c] Reference 3.
[d] Reference 25.
[e] Reference 26.
[f] Reference 27.
[g] Reference 28.
[h] Reference 29.
[i] Reference 30.

Also included in Table I are values for the activation

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energy for the motion of anion vacancies in each salt and the activation energies for $F \rightarrow M$ conversion in KBr via both mechanisms using the models of Asai and Okuda. The thermal ionization energy of the F' center was taken from the photostimulated-thermoluminescence data of Scaramelli.[29] Agreement of the computed values with experiment for KBr is poor, but perhaps agreement is not expected. If covalency is involved in α-center diffusion, the calculated values (last two rows of Table I) should be higher than the observed values (first row). Both mechanisms satisfy such an equality.

By working at a fixed temperature and varying the pressure one gets the activation volume for a process as kT times the derivative with respect to pressure of the logarithm of the rate constant. The slopes of the linear portions of the curves of Fig. 1 are proportional to the rate constant. The logarithms of the slopes were plotted against pressure. A fair straight line resulted, whose slope gave the activation volume to within 20%, based on the scatter. This was done for KCl (two runs) and for CsBr with the results shown in Table II. The two values for the activation volume in KCl differ by more than one expects from an estimate based on scatter. The origin of such run-to-run differences is not known. Similar problems arise in determining activation energies and may account for the discrepancies in the values reported in the literature for F-to-M photoconversion in KCl. These data were taken using a sapphire-windowed high-pressure cell using helium for a pressure fluid.

The activation volumes for vacancy motion have been measured only for cation vacancies.[31] However, Keyes[32,33] has shown that these activation volumes can be correlated roughly with the corresponding activation energies by use of an equation derived on the assumption that the activation energy can be viewed as polarization energy in a dielectric continuum or as strain energy in an elastic continuum. Experimentally, these quantities correlate very well for vacancy diffusion in metals and cation-vacancy motion in dielectrics.[33] We have used Keyes's model to find expected activation volumes ΔV^* for anion-vacancy motion and F-to-M conversion, (Table II) using the equations

$$\Delta V^* = 2(\gamma - 1)KE$$

and

$$\Delta V^* = \left[\left(\frac{\partial \ln\epsilon}{\partial \ln V}\right)_T + \tfrac{1}{3}\right]KE,$$

where K is the compressibility, γ is the Grüneisen constant, and ϵ is the static dielectric constant. $(\partial \ln\epsilon/\partial \ln V)_T$ is known from the work of Mayberg.[34] The two equations give identical results to one significant figure.

TABLE. II. Activation volumes (cm^3/mole).

Process	KCl	KBr	CsBr
F-to-M conversion measured	3.2, 5.1	...	2.7
F-to-M conversion calculated	4.5[a]	6.6[b]	2.0[c]
Anion-vacancy jump calculated	12	14–17	5.4

[a] Using $E = 0.38$ eV.
[b] Using $E = 0.4$ eV.
[c] Using $E = 0.1$ eV.

One can see that the measured activation volumes are small and can be estimated fairly well from the activation energies. This is surprising, for the equation of Keyes has rarely been successful for systems that cannot be treated classically in some fashion.[34] In the present case, we hardly expect to be able to predict ΔV from E when part of E involves either a covalent bond or the ionization of an F' center. In fact, for such systems the term "activation volume" is misleading, for it may not represent a change in size of the system.

In summary, we can say that the activation energy for F-to-M photoconversion is anomalously low in KCl, KBr, and CsBr. The mechanisms proposed to account for such a low energy are not yet very convincing, although in the special case of LiF, M^+ centers have been seen during F-to-M conversion. The activation volumes for this process are very small.

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