splitting, effective masses, x-ray form factors, and the effects of hydrostatic pressure on the bands.

These results are based almost completely on first principles with no adjustment to fit experiment. The only experimental datum used is the lattice constant. Correlation is neglected and Slater's exchange approximation is made. In the final analysis, the validity of these results depends upon the applicability of Slater's exchange approximation, the validity of the SCOPW model, and the convergence of the wave-function expansions. Past experience on many tetrahedral compounds gives us considerable faith in the validity of these results.

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Formation of *I* Centers in LiF under Electron Irradiation*

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The lithium interstitial model (antimorph of the *H* center) for the defect associated with the 5430-Å absorption band formed in LiF by electron or neutron irradiation at 77 °K is strongly supported by new experimental results: The creation rate of these defects is proportional to the incident electron flux, is independent of the *F*-center creation rate, and increases with the thickness of the sample, in good agreement with a knock-on process.

I. INTRODUCTION

An absorption band at 5430 Å is formed in LiF irradiated with neutrons or electrons at 77 °K.[1,2] This so-called *I* band was tentatively assigned to a primary radiation defect not previously observed, the lithium interstitial center. The present paper reports additional experiments on the formation of this center which support this assignment.

The *I* band is shown in Fig. 1. The band appears only for large doses of irradiation (integrated flux greater than $5\times10^{15} n/cm^2$ for neutrons and $5\times10^{16} e/cm^2$ for electrons). The growth of the band is linear with dose in this range, is only slightly dependent on impurity concentration, and also can occur at higher temperatures (thermal bleaching occurs at 400 °K).[2]

An emission band at 9000 Å is associated with the *I*-band absorption. Polarization measurements of the luminescence with polarized excitation light indicated that the defect is oriented along ⟨110⟩ or ⟨121⟩ directions.[1] The zero-phonon line between these mirror bands cannot be observed. Half-widths and positions of the *I* absorption and emission bands indicate that there is strong vibrational coupling. The isotope shift of the absorption band between Li^7F and Li^6F ($\overline{E}_7 - \overline{E}_6 = 0.003$ eV) implies that the coupled modes involve primarily lithium ions.[3]

The defect model proposed for the *I* center is the so-called "lithium interstitial" center. An impurity center seems improbable because the formation appeared to be quite sample independent. An intrinsic defect in the halogen sublattice is excluded because such defects can be formed with ionizing radiation, whereas the *I* center cannot. A knock-on process can cause a defect in the alkali lattice. A vacancy center in the alkali lattice, such as the V_F antimorph of the *F* center, is ruled out because its absorption should be in the ultraviolet.

We thus proposed that the defect is an alkali atom interstitial forming a Li_2^+ molecular ion with the molecular axis in a ⟨110⟩ direction (antimorph of the *H* center). The observed transition could be the $\Sigma_g - \Sigma_u$ transition of Li_2^+ only slightly perturbed by the lattice. This assumption is in agreement with a rough estimation of the transition energy which we made using Wind's results[4] for the isolated molecular ion. Wind has calculated the binding energy of the ground state (bonding state) and found 1.38 eV. Assuming that the energy between bonding and antibonding states ($\Sigma_g - \Sigma_u$) is twice the binding energy, we obtained 2.76 eV, a value quite close to the 2.2 eV observed experimentally.[2] The thermal stability of the defect is also in agreement with our estimate.

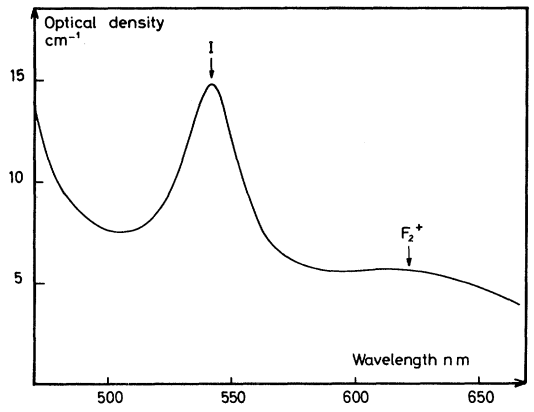

FIG. 1. *I*-band absorption in LiF at 77 °K, after irradiation with 1.5-MeV electrons at the same temperature (dose: 1.1×10^{17} e/cm^2).

If the binding energy is half of the transition energy (i.e., 1.1 eV), then the defect would become unstable above 400 °K as we observed experimentally. At this temperature, we also know that lithium platelets appear in neutron-irradiated samples.[5]

This model is supported by calculations which indicate that such a defect would be stable in LiF. Mourad[6] calculated the energy for the ground state of a substitutional Li_2^+ molecular ion in the ⟨110⟩ direction using a method similar to that used by Das, Jette, and Knox[7] to study the V_K center in LiF. He calculated for various internuclear distances the energy of the valence electron of Li_2^+, the change of the Born repulsion of the lattice, and the change of the electrostatic energy of the lattice when a lithium ion of the lattice is replaced by Li_2^+. The second term was calculated considering the interaction of the displaced ion with its six nearest and twelve next-nearest neighbors. He found that the defect would be stable, the minimum energy being given for an internuclear distance of 2.02 Å. More recently, Fischer and Kemmey[8] did more complete calculations for the ground state and several excited states, taking into account the relaxation of a large number of ions around the defect. They found like Mourad that such a defect would be stable, but they calculated that the energy of the $\Sigma_g - \Sigma_u$ transition is only 0.9 eV instead of the 2.30 eV for the absorption band that we observed experimentally. Their calculations on this point are in disagreement with the model that we suggested.

In the present paper, we report further experiments on the formation of *I* centers to test the hypothesis that a knock-on process is involved. These experiments involve the dependence on

dose, sample thickness, and sample orientation for 1.5-MeV electron irradiation of LiF at 77 °K, and a qualitative experiment on the effect of temperature.

II. EXPERIMENTAL TECHNIQUES

Most of the measurements were performed with 1.5-MeV electrons at liquid-nitrogen temperature. Electrons were provided from a Dynamitron accelerator, and the electron flux at the crystal was monitored with a technique previously described.[3]

Samples were held in a small nitrogen bath formed with two thin tantalum foils (cf. Fig. 2). Liquid nitrogen was supplied continuously to the bath which stood in air at a distance of 2.5 cm from the accelerator window. The sample holder and the bath could rotate about a vertical axis to change the angle of incidence of the beam on the sample.

After irradiation, the sample on its holder was quickly transferred to a liquid-nitrogen immersion optical cryostat and its absorption spectrum was measured at 77 °K with a Cary 14 spectrophotometer. Harshaw crystals of LiF were used, and these were cleaved into thin slices after a short γ irradiation. The thickness of the samples was between 0.1 and 1.0 mm so that sample heating by the beam would not be a problem.

III. EXPERIMENTAL RESULTS

At 77 °K, the creation of I centers with 1.5-MeV electrons occurs in two stages as shown in Fig. 3. The first stage corresponds to an incubation period and the second to the linear growth period. If we use Smakula's equation[9] to estimate the concentration of I centers from the optical density (with the assumption that the oscillator strength

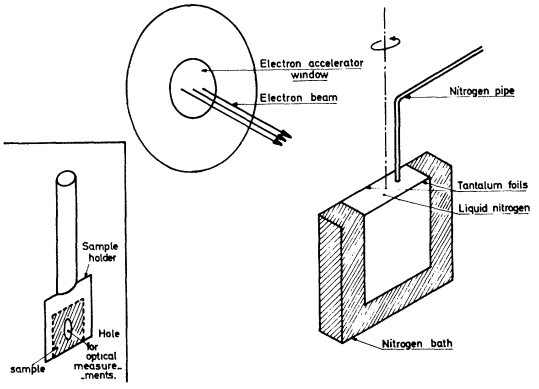

FIG. 2. Electron-irradiation apparatus.

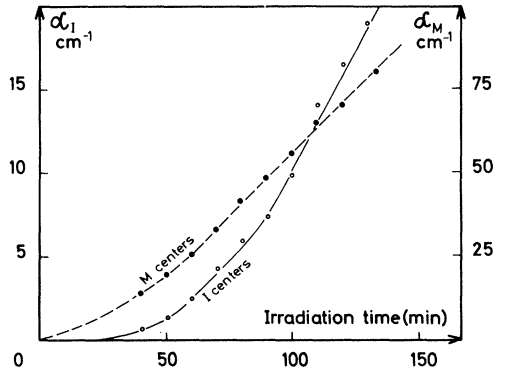

FIG. 3. Creation curves for I and M centers in LiF at 77 °K for 1.5-MeV electrons (flux: 3.75 μA cm^{-2} sec^{-1}).

is one), then the I-center concentration of Fig. 3 is $\sim 1.3\times 10^{16}$ cm^{-3} after 100 min. Similarly, the linear growth rate corresponds to one I center formed per 5.6-MeV incident flux at this energy.

For comparison, the M-center growth curve is shown in Fig. 3. This also shows an incubation period and a linear growth stage, but the concentrations are considerably higher. The F-center concentration was so high that the F band could not be measured directly. However, the F-center concentration can be inferred from the M-center concentration, since at this temperature M centers can be formed only when F centers are created at neighboring sites.[10] Thus $n_M = Kn_F^2$, where n_M is the concentration of M centers, n_F is the concentration of F centers, and K is a geometrical factor ($K \sim 6/N$, N being the total number of halogen ion sites per unit volume of crystal). Thus the M-center growth curve in Fig. 3 indicates that in the initial stage, where n_M is proportional to the square of the time of irradiation, the F-center concentration increases linearly with time. When n_M becomes proportional to time, then n_F must be proportional to $t^{1/2}$, as it is at room temperature.[11]

Figure 4 shows the creation of I centers versus the electron-beam intensity, for a fixed irradiation time at 77 °K [curve (a) 40 min, curve (b) 50 min]. These curves show the same two-stage growth, with the second stage linear in the integrated flux of electrons.

A few qualitative measurements were made at higher temperatures. With the high electron flux used in these experiments, attempts to cool the sample with cold nitrogen gas were inadequate. Instead, to obtain temperatures above 77 °K, the sample was wrapped in very thin aluminum foil and then placed in the nitrogen bath. This method is not precise, but does give some qualitative in-

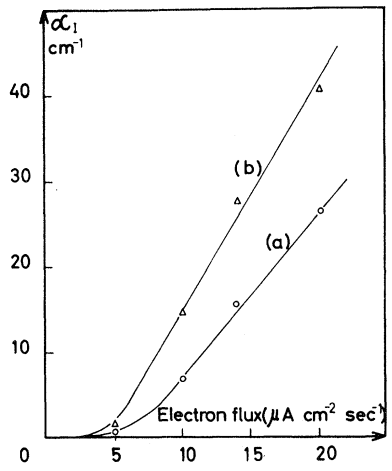

FIG. 4. Creation curve for I centers versus the beam flux of 1.5-MeV electrons after (a) 40 min and (b) 50 min of irradiation.

formation on temperature effects. Figure 5 shows the I-center growth curves for samples at 77 °K (a) and above 77 °K (b). One can see that the incubation period is strongly reduced in samples irradiated above 77 °K. It also appears that the linear part has practically the same slope as at 77 °K, implying that the linear creation rate is temperature independent. The M-center growth curves showed similar changes, with a corresponding reduction in the incubation period.

If, after irradiation at 77 °K, a crystal containing I centers is warmed to room temperature, a large number of F-aggregate centers are formed and these partly obscure the I band. If the crystal is then cooled to 77 °K and reirradiated, these complex centers disappear very rapidly and the I band can be observed with the same intensity

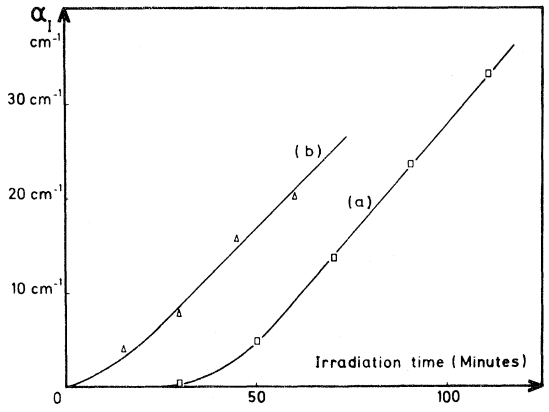

FIG. 5. Creation curve for I centers with 1.5-MeV electrons (flux: 7.5 μA cm^{-2} sec^{-1}) (a) at 77 °K and (b) above 77 °K.

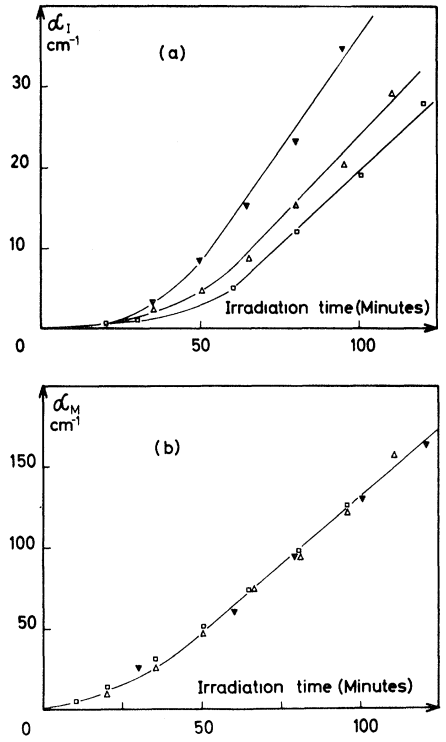

FIG. 6. Creation curves for I and M centers at 77 °K in three LiF samples with different thicknesses; □, 0.10 mm; △, 0.20 mm; ▼, 0.97 mm. Irradiation time was 50 min at 7.5 μA cm^{-2} sec^{-1} with 1.5-MeV electrons.

as just after the original irradiation.

At 77 °K, the density of I centers formed depends on the thickness of the sample. Figure 6(a) shows this effect for three different crystals, of thickness 0.10, 0.20, and 0.97 mm. The thinner the crystal, the smaller the number of I centers formed per unit volume. In Fig. 6(b), one can see that the density of M centers formed is independent of thickness in this range. Earlier measurements[3] showed that the F-center density is also approximately constant for this thickness range with 1.5-MeV electrons. Figure 7 summarizes the results for the thickness dependence of the I-center density formed under identical irradiation conditions (50 min at 77 °K with 7.5 μA cm^{-2} sec^{-1} of 1.5-MeV electrons).

We have not observed any significant angular dependence of the I-center creation rate at 77 °K. With the same electron flux and the same irradiation time, the number of I centers formed was the same whatever the angle of incidence in the range from $\theta = 0°$ (normal) to $\theta = 50°$. Since the crystals were thin the reduction of the flux on the sample [$\phi(\theta) = \phi_0 \cos\theta$] was just compensated by the increase in path length in the crystal [$d(\theta) = d_0/\cos\theta$]. We did observe some angular depen-

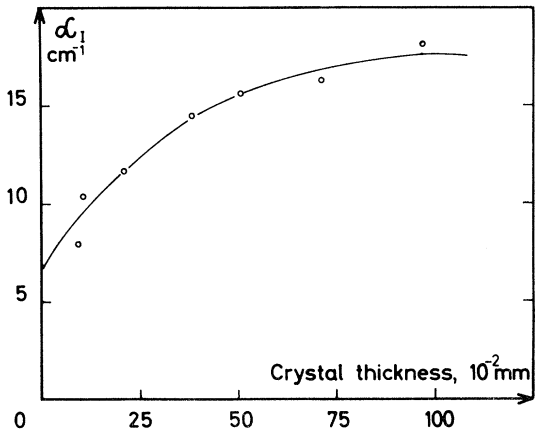

FIG. 7. Variation of the density of I centers formed with sample thickness. Irradiation conditions were the same as in Fig. 6.

dence for samples irradiated above 77 °K, but this effect may well be correlated with a change in the heating of the sample.

IV. INTERPRETATION

The I-center creation rate should be proportional to the incident electron flux if these centers are formed directly by a knock-on process between an incident electron and a Li^+ ion of the lattice. The observed creation rate is linear and independent of temperature following an initial incubation period whose duration depends on temperature.

The linear creation rate agrees with that found earlier[2] and corresponds to 0.33 I center formed per incident electron of 1.5-MeV energy. This is very much less than the number of F or M centers formed. This creation efficiency is in order of magnitude agreement with our earlier estimate which assumed a displacement energy of 10 eV for the lithium ion.[2]

The thickness dependence of the linear creation rate (cf. Fig. 7) is also consistent with a knock-on process. It is well known that the energy of electrons decreases continuously after their entrance into the crystal.[12] It is also well known that the total displacement cross section (primaries and secondaries) varies with the energy of electrons. For small displacement energies (< 10 eV) and light atoms, this cross section has a maximum at the threshold energy and then decreases as the energy increases.[13] For example, using Rutherford's formulas, the cross section at the threshold energy is three times larger than at 1.5 MeV in beryllium with a displacement energy E_d of 5 eV; for carbon, with $E_d = 5$ eV, the ratio is 1.9 between the two cross sections.[14] In our case the thinner the sample, the higher the mean energy of electrons in the volume and the smaller the number of I centers formed in the same mass of crystal.

The incubation period is somewhat more difficult to understand. The observation is that the incubation period decreases with increasing temperature, and is roughly comparable to the duration of linear F-center production; i.e., the "incubation period" before linear M-center production. We will discuss two possibilities.

First, we can imagine that the free-ion (or free-atom) interstital is very mobile just after its creation, before an electronic relaxation which could give rise to the Li_2^+ molecular ion. In this case, this free interstitial could be trapped by some chemical impurities and the creation rate would be linear only when all these traps were filled. The difference between the linear part and the actual growth curve would decrease exponentially with irradiation time as experimentally observed. In this case, the interstitial-impurity complex would have to be thermally stable under 200 °K. We observed no change of the I-center density in a crystal irradiated at 77 °K with an irradiation time corresponding to the incubation period when it was warmed to 200 °K.

A second alternative is based on the correlation between the incubation and linear F-center production. As we suggested in an earlier paper[11] the change in the F-center creation rate is very probably correlated with a change in the configuration of halogen interstitials. At the beginning of the irradiation at 77 °K, halogen interstitials form small aggregates such as V_1, V_4, etc. After a long irradiation time they form bigger aggregates increasing in size but not in number. At temperatures above 77 °K the linear rate of F centers is not observed because the aggregation process of interstitials is faster. In this case, lithium interstitials could be trapped by very small halogen interstitial clusters; the lower the temperature the higher the probability of such a trapping. For example, a Li^+ interstitial could be trapped by a V_1 center to form a LiF interstitial molecule associated with an alkali impurity.

The definite cause of the incubation period for I-center growth cannot be specified on the basis of present information.

The final experimental observation, that the linear creation rate is essentially independent of angle of incidence of the electron beam, contradicts a result of our earlier experiments.[15] However, in that case, the angular dependence was correlated with a variation of sample temperature with angle of incidence and was probably spurious.

A variation in creation rate with angle could be expected if the primary electrons create focused

collision sequences. Calculations for such processes have been done by Balarin[16] and more recently by Torrens and Chadderton.[17] Unfortunately, the more complete calculations of Torrens and Chadderton have not been performed for LiF crystals. Balarin determined the energy limit E_F above which defocusing occurs. He calculated E_F for focused collision sequences in the halide sublattice and he found 8.5 eV. The lithium ionic radius being smaller than the fluorine radius, E_F would be smaller for sequences in the alkali sublattice. The maximum energy T_{max} which can be transferred to a lattice atom in an elastic collision with an electron is

$$T_{max} = 2(E_e + m_e c^2) E_e / Mc^2, \quad (1)$$

where E_e is the incident electron energy, M and m_e are the mass of the target atom and the electron, respectively, and c is the velocity of light. Hence, a 1.5-MeV electron can impart a maximum recoil energy of 560 eV to a lithium ion. This is too large to have focused collision sequences, so lithium ion displacements should be nearly independent of the incidence angle of electrons under the conditions of our experiments.

V. CONCLUSION

The lithium interstitial model for the I center which gives rise to the 5430-Å absorption band in LiF is supported by new experiments on the formation rate under 1.5-MeV electron irradiation at 77 °K. Two growth stages are involved: an incubation period and a linear stage. The linear rate is of the right magnitude for a knock-on process, is independent of temperature, and does depend on sample thickness. The absence of any dependence on the angle of beam incidence is consistent with the relatively large incident energy of the electrons, well above the defocusing limit.

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