

## Extreme Ultraviolet Absorption by Lithium Fluoride\*

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A study was made to determine the absolute value of the absorption coefficient for lithium fluoride between 10 and 110 ev. The first exciton level in the fundamental absorption was found to be at 12.9 ev. Absorption structure attributed to the fluorine 2s electrons and lithium 1s electrons was observed. The energy band gap was estimated to be less than 14 ev. The absorption structure associated with the Li K electrons was found at energies corresponding to transitions by the 2s electrons of the free  $\text{Li}^+$  ion. A duplication of this structure at a higher energy suggested the possibility that a multiple process was involved in the photon absorption.

### I. INTRODUCTION

ULTRAVIOLET absorption studies have been of considerable value in examining the structure of the excited states in the alkali halides. Many experimental studies have been made on the alkali halide materials in the region of their fundamental optical absorption.<sup>1-3</sup> However, little work has been done at higher photon energies in the vacuum ultraviolet. Toward higher photon energies, the optical absorption should show structure due to absorption by electrons in shells of the constituent atoms of the solid. A determination of the absolute absorption coefficient provides information about the energy level scheme for these electrons. The study of photon absorption by bound electrons in solids has been reviewed by Skinner<sup>4</sup> and more recently by Tomboulou<sup>5</sup> and Parratt.<sup>6</sup>

In the present work the absorption spectrum of solid LiF was studied in the energy range of 10 to 110 ev. The fundamental optical absorption is located in this energy range. From the optical absorption spectrum an upper limit to the value of the energy band gap could be estimated. The shape of the absorption curve for the higher energy region was used to estimate the energy width of the conduction band. An optical effect due to a plasma effect was sought.<sup>7</sup>

### II. EXPERIMENTAL PROCEDURE

The samples used in this investigation were prepared by vacuum evaporation upon thin (50 to 250 Å thick) celluloid substrates. The evaporations were carried out at pressures of about  $5 \times 10^{-5}$  mm Hg and from a platinum boat heated electrically to about 900°C. Two samples of different thickness were prepared in each

evaporation and simultaneously two monitoring samples were deposited on an optical flat. The thicknesses of the monitoring samples were subsequently determined by multiple-beam interferometry.<sup>8</sup> The absorption coefficient was determined by observing the difference in transmission of the two samples. In order to diminish the effect of the sample-substrate interface,<sup>9</sup> the thinner sample was always made more than 30 Å thick.

The structure of LiF films formed by vacuum evaporation onto celluloid has been analyzed by electron diffraction.<sup>10,11</sup> These studies indicated the presence of internal voids and surface irregularities, resulting in a decrease in average density from the usual bulk value. The multiple-beam interferometry measurements determine the physical thickness of this porous sample.

The grazing incidence vacuum spectrograph used in this investigation has been described earlier,<sup>12</sup> and consists of a 30 000 line-per-inch concave grating used at 85° angle of incidence and with a Rowland circle of one-meter radius. The source was a Lyman-type discharge tube similar to that described by Rathenau.<sup>13</sup> Argon, helium, and a mixture of helium and neon were used in the source to obtain lines through the spectral region studied. In addition to lines produced by these gases, there were also lines due to silicon and oxygen from the walls of the quartz capillary source and lines of nitrogen presumably from residual air. These lines were identified by comparison with published tables<sup>14</sup> and used to establish the wavelength scale.

Argon and helium were used not only as source gases but also as filters.<sup>15,16</sup> When used at pressures of a few mm Hg these gases are opaque to wavelengths shorter

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<sup>1</sup> R. Hilsch and R. W. Pohl, *Z. Physik* **59**, 812 (1930).

<sup>2</sup> E. G. Schneider and H. M. O'Bryan, *Phys. Rev.* **51**, 293 (1937).

<sup>3</sup> J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959).

<sup>4</sup> H. W. B. Skinner, *Repts. Progr. in Phys.* **5**, 257 (1938).

<sup>5</sup> D. H. Tomboulou, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 246.

<sup>6</sup> L. G. Parratt, *Revs. Modern Phys.* **31**, 616 (1959).

<sup>7</sup> W. C. Walker, O. P. Rustgi, and G. L. Weissler, *J. Opt. Soc. Am.* **49**, 471 (1959).

<sup>8</sup> S. Tolansky, *Multiple-Beam Interferometry of Surfaces and Films* (Oxford University Press, New York, 1948).

<sup>9</sup> D. H. Tomboulou and E. M. Pell, *Phys. Rev.* **83**, 1196 (1951).

<sup>10</sup> L. G. Schultz, *J. Chem. Phys.* **17**, 1153 (1949).

<sup>11</sup> J. S. Halliday, T. B. Rymer, and K. H. R. Wright, *Proc. Roy. Soc. (London)* **A225**, 548 (1954).

<sup>12</sup> M. P. Givens and W. P. Siegmund, *Phys. Rev.* **85**, 313 (1952).

<sup>13</sup> G. Rathenau, *Z. Physik* **87**, 32 (1933).

<sup>14</sup> R. Kelly, University of California Radiation Laboratory Report, UCRL-5612, Stanford Research Institute, California, 1959 (unpublished).

<sup>15</sup> P. Lee and G. L. Weissler, *Phys. Rev.* **99**, 540 (1955).

<sup>16</sup> N. Wainfan, W. C. Walker, and G. L. Weissler, *Phys. Rev.* **99**, 542 (1955).

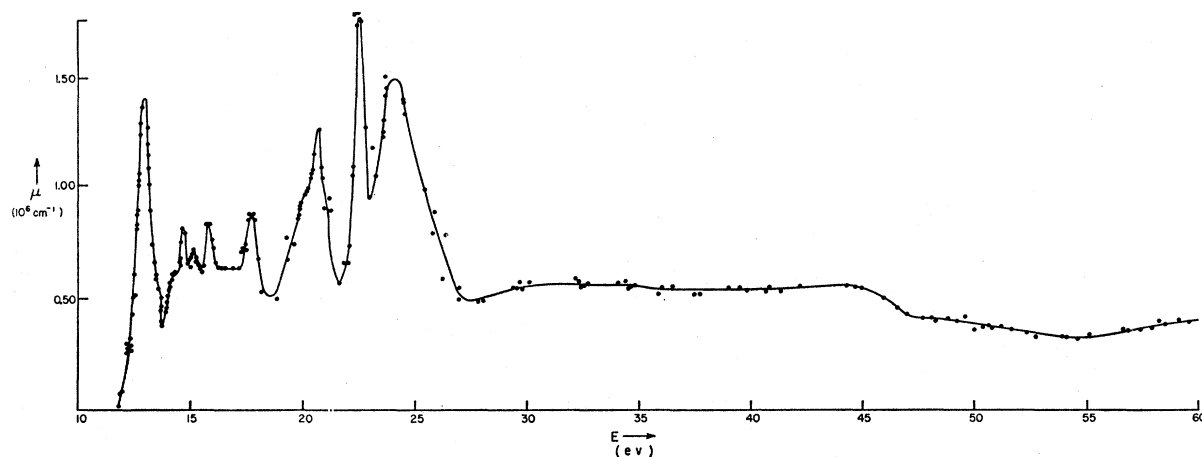


FIG. 1. Absorption coefficient of lithium fluoride in the photon energy range between 10 and 60 ev.

than 780 and 504 Å, respectively. Their use as filters greatly simplifies the problem of overlapping orders.

Exposures, through samples of two different thicknesses, were made on adjacent areas of spectroscopic plates (Kodak SWR or Ilford Q) and the data reduced by a method of comparison developed by Cady and Tomboulion.<sup>17</sup> Application of the method to absorption work has been described earlier.<sup>18</sup> This method of photographic photometry together with the difference in the measured thicknesses of the samples was sufficient data to calculate the absorption coefficient as a function of wavelength or photon energy. The use of two films of different thickness, rather than one film and a blank substrate results in an automatic correction for reflection loss.

The absorption coefficient  $\mu$  as a function of photon energy  $E$  is given in Figs. 1 and 2.

### III. RESULTS AND DISCUSSION

#### A. Low-Energy Structure

From the figures it is clear that  $\mu$  rises sharply with energy at 11.8 eV, in accordance with the observations on bulk LiF crystals.<sup>19</sup> A narrow absorption band of 0.8-eV full width at half-maximum with an energy maximum at 12.9 eV is associated with the first exciton level. This band appears to be symmetrical about the energy peak. Other recent measurements have placed both the reflectivity peak<sup>20</sup> and the absorption peak<sup>21</sup> at 12.7 eV.

Toward higher energies there is a definite shoulder in the absorption curve between 14.0 and 14.2 eV. Similar shoulders have been observed in other alkali halides.<sup>3</sup> Apker and Taft<sup>22,23</sup> argued that the valence to conduction-band transitions begin at this value, or

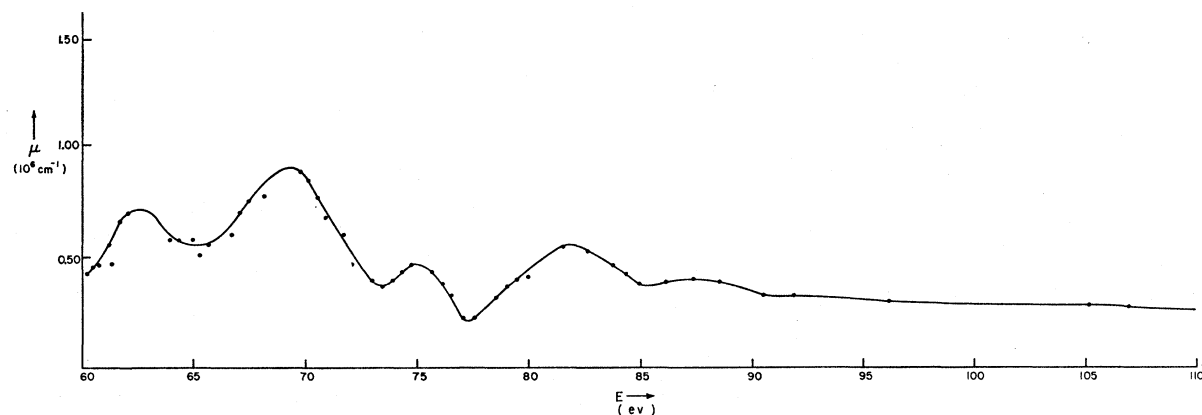


FIG. 2. Absorption coefficient of lithium fluoride in the photon energy range between 60 and 110 ev.

<sup>17</sup> W. M. Cady and D. H. Tomboulion, *Phys. Rev.* **59**, 381 (1941).

<sup>18</sup> W. R. Woodruff and M. P. Givens, *Phys. Rev.* **97**, 52 (1955).

<sup>19</sup> E. G. Schneider, *Phys. Rev.* **49**, 341 (1936).

<sup>20</sup> R. Kato, K. Nakamura, A. Matsui, and Y. Uchida, *J. Phys. Soc. Japan* **15**, 2105 (1960).

<sup>21</sup> R. Onaka, A. Fukuda, and A. Ejiri, *J. Phys. Soc. Japan* **16**, 340 (1961).

<sup>22</sup> L. Apker and E. Taft, *Phys. Rev.* **81**, 698 (1951).

<sup>23</sup> L. Apker and E. Taft, *Phys. Rev.* **82**, 814 (1951).

that this is the value of the energy band gap. It was not possible to resolve the exciton peaks near the alleged series limit because of the intense overlapping. However, peaks were observed at 12.9 and 14.65 ev in accordance with the prediction of hydrogen-like energy levels.<sup>24</sup>

A complex absorption structure was found between 22 and 26 ev. There is a narrow peak of 0.5 to 1.0 ev full width at half-maximum centered at about 22.5 ev. A wide band, possibly containing some unresolved structure has a maximum near 24.3 ev. This latter wide band is associated with electron transitions from the  $F^-$  ion 2s band to the conducting levels. The narrow peak at 22.5 ev is probably an excitation level associated with the  $F^-$  ion 2s band.

### B. Energy Band Gap

The energy separation between the valence band and the band corresponding to the  $F^-$  ion 2s electrons must be known approximately in order to interpret the absorption curve. Emission studies by O'Bryan and Skinner<sup>25</sup> have shown the existence of the 2p band but not the 2s band in LiF. However, they did observe emission in BeO which was due to the oxygen 2s and 2p bands. For BeO, which resembles LiF electronically, the 2s-band to 2p-band energy separation (peak to peak) has nearly the same value for the solid state as for the free oxygen ion.<sup>26</sup> On this basis the 2s to 2p separation in LiF can be estimated by referring to the energy levels corresponding to the s and p electrons of the  $F^-$  ion. The use of this method<sup>27</sup> leads to an estimate of 12.6 ev for the energy separation. This can be compared with the theoretical value of 10.8 ev derived by Ewing and Seitz.<sup>28</sup>

The form of the density of states curve for the valence band has been measured experimentally by emission spectroscopy.<sup>25</sup> The half-width of the emission curve for LiF was found to be 2.0 to 2.5 ev. Grimley<sup>29</sup> computed the half-width of the  $F^-$  ion 2p valence band to be 2.7 ev. Ewing and Seitz<sup>28</sup> calculated the energy vs wave-number curves for the energy bands corresponding to the  $F^-$  ion 2s and 2p electrons and for the first-empty band corresponding to a  $Li^+$  ion 2s electron. They predicted a half-width of about 2.5 ev for the valence band, about 0.2 ev for the half-width of the next lower energy band which corresponds to the  $F^-$  ion 2s electrons, and about 1 ev for the half-width of the first empty band.

According to atomic selection rules, the final state for an electron ejected by the absorption process from

the  $F^-$  ion 2s band is not the same as the final state for an electron ejected from the 2p band. Utilizing the known electron energy structure it could be stated that

$$E_g + y + x + Z = V,$$

where  $E_g$  is the energy band gap,  $y$  is the separation between the bottom of the conduction band and the first-allowed state for a 2s-band electron transition,  $x$  is the peak-to-peak separation of the  $F^-$  2s to 2p bands,  $Z$  is the half-width of the valence 2p band, and  $V$  is the energy separation between the  $F^-$  2s band and the first-allowed energy level for a  $F^-$  2s electron transition.

As stated previously,  $Z = 2.5$  ev, and  $x$  is between 10 and 13 ev. To get an upper limit for  $E_g$ , take  $x > 9$  ev. Experimentally, it was seen from Fig. 1 that  $V \leq 25.5$  ev. Then,

$$E_g < E_g + y \leq 25.5 - 2.5 - 9 = 14$$

or

$$E_g < 14 \text{ ev.}$$

Measurements of the threshold for photoconductivity should provide supplementary information concerning the energy band gap. Taylor and Hartman<sup>30</sup> did not observe any photoconductivity for a number of alkali halides including KI and LiF. They did observe that the photoemissive threshold for LiF was near 12 ev, which, referring to Fig. 1, is in the low-energy foot of the first exciton peak. They also observed a small peak in the photoelectric yield at 13.0 ev, which, referring to Fig. 1, corresponds to the first optically observed exciton peak. It appeared that the optical absorption curve was similar to the photoelectric emission yield curve for LiF in the low-energy region. Apker and Taft<sup>22</sup> have observed a similar behavior with RbI, and have attributed this effect to an exciton transferring energy to an  $F$  center, with a subsequent ionization of the  $F$  center causing photoelectric emission. Taylor and Hartman<sup>30</sup> tentatively placed the valence band in LiF at about 13 ev below the vacuum level, on the assumption that the photoelectric threshold is almost the energy of the band gap.

Mott and Gurney<sup>26</sup> calculated the energy  $W$  necessary to remove an electron from the valence band to the vacuum level by considering a very simple charge-transfer cycle. The value  $W$  for LiF was found to be about 13.5 ev, implying that the energy band gap was less than 13.5 ev.

### C. Plasma Loss

An electron traversing a thin solid foil has been found to lose discrete amounts of energy.<sup>31,32</sup> The characteristic energy loss  $E$  is predicted to be given by

$$E = \hbar(4\pi ne^2/m)^{1/2}.$$

<sup>30</sup> J. W. Taylor and P. L. Hartman, *Phys. Rev.* **113**, 1421 (1959).

<sup>31</sup> L. Marton, *Revs. Modern Phys.* **28**, 172 (1956).

<sup>32</sup> H. Watanabe, *J. Phys. Soc. Japan* **9**, 920 (1954).

<sup>24</sup> G. H. Wannier, *Phys. Rev.* **52**, 191 (1937).

<sup>25</sup> H. M. O'Bryan and H. W. B. Skinner, *Proc. Roy. Soc. (London)* **A176**, 229 (1940).

<sup>26</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1948).

<sup>27</sup> A. A. Milgram, Ph.D. dissertation, University of Rochester, 1961 (unpublished).

<sup>28</sup> D. H. Ewing and F. Seitz, *Phys. Rev.* **50**, 760 (1936).

<sup>29</sup> T. B. Grimley, *Proc. Phys. Soc. (London)* **71**, 749 (1958).

TABLE I. The ground state of  $\text{Li}^+$  and states which can be reached by a single transition.<sup>a</sup>

Configuration	Energy state	Energy (ev)
$1s^2$ (ground state)	$^1S_0$	75.3
$1s2p$	$^1P_1$	13.4
$1s3p$	$^1P_1$	5.96
$1s4p$	$^1P_1$	3.36
$1s5p$	$^1P_1$	2.15

<sup>a</sup> Extracted from R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932), pp. 266-7.

The assumption has been made for the alkali halides that the average number of valence electrons per atom is four.<sup>31</sup> Using this model, the calculated energy loss for LiF is about 26 ev.

The optical absorption curve showed structure associated with the  $\text{F}^-$  2s band between 26 and 27 ev, and thus obscured any possible plasma effect.

#### D. High-Energy Structure

The position of the  $\text{Li}^+$  ion levels in the solid was estimated by referring to a table of energy levels for free ionic  $\text{Li}^+$ . The ground state of the free  $\text{Li}^+$  ion has the  $1s^2$  electron configuration and gives rise only to a  $^1S_0$  state. For a one-electron jump, the possible configurations are  $1s2s$ ,  $1s2p$ ,  $1s3s$ ,  $1s3p$ , etc.

Restrictions on the possible transitions using atomic selection rules allow only transitions involving the energy states shown in Table I.

Between 60 and 100 ev, structure was found which was due to absorption by the  $\text{Li}^+$  ion 1s electrons. Absorption peaks were found at  $62.5 \pm 0.5$  ev and  $69.0 \pm 0.5$  ev. These energies correspond to the energy differences between the ground state and the first two

excited states of the  $\text{Li}^+$  ion shown in Table I. A similar situation was observed by O'Bryan<sup>33</sup> for the  $L$  absorption by sodium in the sodium halides.

Other peaks were found at  $75.0 \pm 0.5$  ev and  $82.0 \pm 0.5$  ev and there was an indication of a peak near 87.5 ev. The absorption structure between 61 and 73 ev appeared to be duplicated between 74 and 86 ev, suggesting a multiple absorption process. The peaks at 62.5 and 75.0 ev both had a full width at half-maximum of  $3.5 \pm 0.5$  ev. The peaks at 69.0 and 82.0 ev both had a full width at half-maximum of  $4.8 \pm 0.7$  ev. These widths correspond to the bandwidths of the states of predominantly  $p$ -type character in the conduction band. The ratio of the height of the absorption structure between 61 and 73 ev to that between 74 and 86 ev was found to be  $1.2 \pm 0.1$ . This suggests that the cross sections for the two events are comparable, which would not be expected if one is a simple absorption process and the other a multiple process.

A multiple absorption process involving the transition of a  $\text{Li}^+$  1s electron to a higher level and the production of an exciton due to excitation of the  $\text{F}^-$  ion 2p electron would involve a shift of the absorption curve by 12.9 ev, the first exciton level energy. Emission spectra of the alkali halides have shown in many cases a duplication of the characteristic features at energy separations equal to the exciton energy.<sup>25</sup> Townsend<sup>34</sup> has investigated the Mg  $L$  absorption in MgO. He observed an absorption structure between 54 and 76 ev which appeared to be duplicated at 17-ev higher energy. It can be shown that for MgO the excitation of an oxygen ion 2s electron would require about 20 ev.

<sup>33</sup> H. M. O'Bryan, Phys. Rev. **57**, 995 (1940).

<sup>34</sup> J. R. Townsend, Phys. Rev. **92**, 556 (1953).