

Core excitons at the  $K$  edge of LiFJ. P. Stott,\* S. L. Hulbert,<sup>†</sup> F. C. Brown, B. Bunker,<sup>‡</sup> T. C. Chiang, and T. Miller*Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

K. H. Tan

*Canadian Synchrotron Radiation Facility, Physical Sciences Laboratory, Stoughton, Wisconsin 53589*

(Received 15 July 1983)

The lithium core-exciton spectrum has been reinvestigated with high resolution using synchrotron radiation. Photoelectron yield techniques were employed on evaporated thin films and single crystals cleaved in ultrahigh vacuum. The various observed structures can be well correlated with the results of recent cluster calculations which incorporate multiplet splitting. Photoemission data and the observed band gap are used to estimate the threshold for transitions to the continuum (additivity). The binding energy of the 61.9-eV  $^1\Gamma_{15}$  core exciton is found to be 2.1 eV. A lower 58-eV  $^3\Gamma_1$  core exciton is observed to have a 6-eV binding energy. In addition, interesting results are obtained which are believed to be due to the generation of point defects ( $F$  centers) and aggregates following exposure to intense undispersed synchrotron radiation.

## I. INTRODUCTION

The photoexcitation of LiF at about 60 eV produces perhaps the simplest of cation defects, namely a lithium core exciton. Detailed spectra above this vacuum ultraviolet threshold have been obtained by a variety of different experimental techniques including photoabsorption by thin films,<sup>1-3</sup> electron yield,<sup>4</sup> x-ray luminescence,<sup>5</sup> thermomodulation,<sup>6</sup> and electron energy loss.<sup>7</sup> A number of discrepancies exist in the literature cited above especially as regards to the existence of a threshold and weak structure at about 58 eV which is 3 or 4 eV below the strong core-exciton absorption line generally observed at 61.9 eV. The existence of 58-eV structure is crucial for a detailed interpretation of the spectra in comparison with theory, especially considering earlier,<sup>8</sup> and very recent,<sup>9</sup> high-quality cluster calculations of the ground and excited states involved.

In this paper we report the results of new high-resolution electron yield studies using synchrotron radiation from the storage ring Tantalus at the Physical Sciences Laboratory, Stoughton, Wisconsin. The measurements were carried out in ultrahigh vacuum on both single crystals cleaved *in situ* and thin films evaporated onto metallic substrates.

The actual Li- $K$  absorption threshold is found to be at about 58 eV, and the near-edge features above this threshold can be understood in terms of various excited states including multiplet splitting according to recent theory.<sup>9</sup>

## II. EXPERIMENTAL DETAILS

Angle-integrated photoemission was observed in an ultrahigh vacuum chamber after a refocusing mirror on the Pennsylvania toroidal grating monochromator (TGM) at the small 240-MeV storage ring Tantalus.<sup>10</sup> A spectral bandwidth of about 0.2 eV was employed for photon ener-

gies between 50 and 100 eV. Electron energy was analyzed by means of a double cylindrical mirror analyzer.

The Canadian synchrotron radiation facility (CSRF) was also used as a tunable source of photons in the range 50 to 150 eV. This beam line employs a modified "grasshopper" monochromator<sup>11</sup> with adjustable slits and a toroidal refocusing mirror. A 1200 line/mm grating was used so that the spectral bandwidth (50- $\mu$ m slits) was about 0.08 eV. The intensity and throughput of this beam line compared favorably with the TGM line.

An LSI 11/23 computer was used for control and data acquisition and to scan each of the above monochromators (through a microprocessor-based stepping motor driver system). The data were processed including normalization, smoothing, etc., in a larger computer with extended graphics capability.

Good single-crystal surfaces were achieved by cleaving melt grown crystals of LiF supplied by the Harshaw Chemical Company. Cleaving in ultrahigh vacuum after bakeout and in air just before inserting in the vacuum chamber gave similar results except for minor differences in the valence-band energy distribution curves (EDC). In this regard LiF seems somewhat better to work with than NaCl on which it is reported that a hydroxide layer forms, during bakeout of air cleaved crystals.<sup>12</sup> In all cases single crystals of LiF showed severe charging under photoemission conditions. This could be alleviated to some extent by means of a flood gun filament.

Studies were also made on thin LiF films (about 200- $\text{\AA}$  thick) which were evaporated onto tungsten substrates in a separately pumped sidetube and then inserted into the photoemission chamber. These thin-film samples showed very similar results to the cleaved crystals and they did not charge significantly. We turn to a discussion of the actual data in the next section.

### III. EXPERIMENTAL RESULTS

In Fig. 1 we show an electron energy distribution curve for an incident photon energy of 120 eV. This data was taken with the photoemission chamber on the Canadian beam line with a grasshopper monochromator. The overall instrument resolution including the electron analyzer was about 0.2 eV. In general Fig. 1 shows good agreement with the results of Gudat *et al.*<sup>4</sup> Notice that electron energy is plotted relative to the top of the valence band. The overall valence bandwidth (base width) observed in the present experiment is  $4.0 \pm 0.2$  eV, which can be compared with a width of  $4.6 \pm 0.3$  eV reported by Pong and Inouye<sup>13</sup> and a width computed by A. B. Kunz<sup>14</sup> of 3.1 eV. Notice from Fig. 1 that two peaks in density of states occur, corresponding mainly to where the two bands involved approach the Brillouin zone boundary (see Fig. 2 of Ref. 14). A rather broad fluorine  $2s$  level is to be seen in Fig. 1 at  $-23$  eV. Weak structure previously ascribed to plasmons<sup>4</sup> appears on either side of this band.

The prominent peak at  $-49.5 \pm 0.2$  eV in Fig. 1 is due to photoemission from the Li  $1s$  core level. The observed half width of this line is 1.5 eV, which is much more than the overall experimental resolution of 0.2 eV. It is no doubt determined by several Auger processes in the crystal which have been rather well studied.<sup>15</sup>

Figure 2 shows partial electron yield versus photon energy using a cylindrical mirror analyzer set to accept low-energy secondary electrons in a band about 2 V wide centered at 10 eV. This evaporated LiF film data was taken on the grasshopper monochromator with a spectral resolution in this range of about 0.1 eV. It has been normalized by dividing each point by the observed partial yield of a freshly evaporated gold surface corrected by the published gold yield of Haensel *et al.*<sup>16</sup> Such observations on solid surfaces (total and partial yield) have been shown to faithfully reproduce spectral details of the total photoabsorption cross section near threshold.<sup>17</sup>

The normalized yield data for LiF shown in Fig. 2 is approximately constant with energy in the range 50 to 55

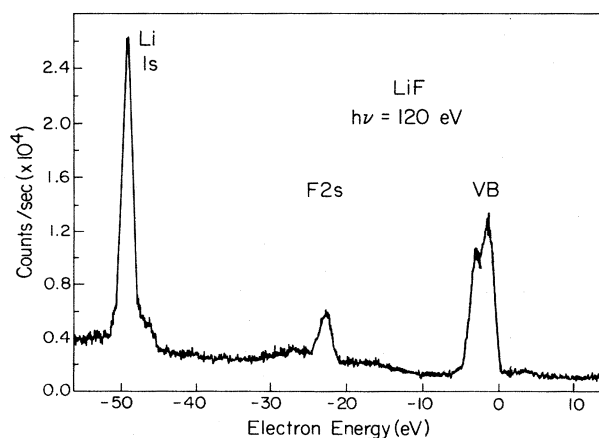


FIG. 1. Electron energy distribution curve for an evaporated LiF film (300 K) illuminated with 120-eV photons. The zero energy is placed at the top of the valence band.

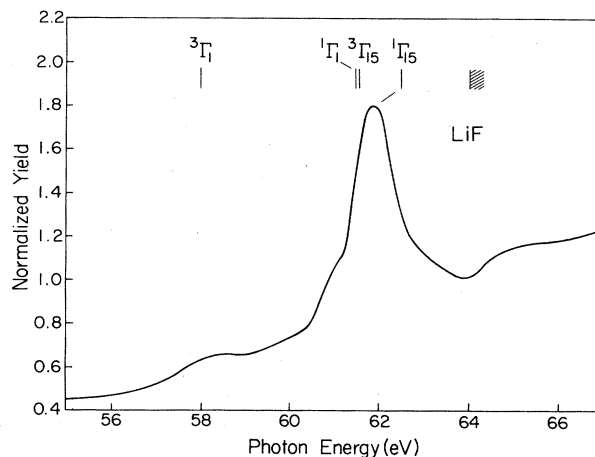


FIG. 2. Yield of 10-eV electrons versus photon energy for LiF (300 K) showing the  $\text{Li}^+$  threshold spectrum. Data have been normalized to constant photon flux. The transition energies from ground to four excited states (Ref. 9) are shown. The transition energy from Li-K to the continuum is shown, by shading, beginning at 64-eV (from data of Fig. 1) and 14.2-eV band-gap energy (Piacentine, Ref. 20).

eV. Notice in Fig. 2 that a rise and faint structure begins around 56–57 eV, as previously reported by Sonntag<sup>3</sup> and by Gudat, Kunz, and Petersen.<sup>4</sup> We believe that this rise (which is very small) probably corresponds to transitions in the vicinity of defects or radiation damage in the crystal. Above the 56–57 eV rise at about 58 eV a just discernible peak occurs. This is followed by the strong main band at  $61.9 \pm 0.1$  eV which has a shoulder on the low-energy side at 60.8 eV. All of these features can be seen in the high-resolution thin-film transmission data of Sonntag.<sup>3</sup>

Figure 3 shows normalized electron yield data very close to threshold on a single crystal of LiF cleaved in ultrahigh vacuum. This data was taken using the TGM

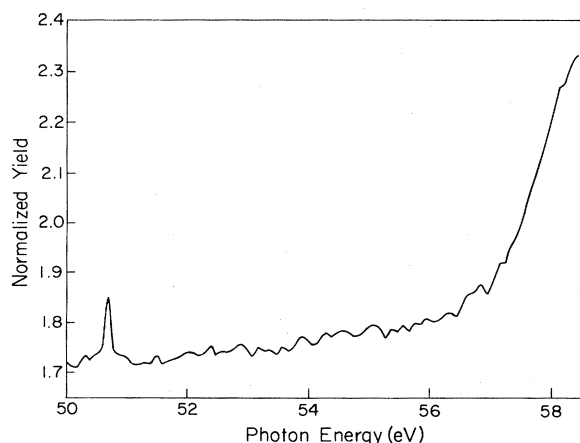


FIG. 3. Normalized yield for 10-eV electrons from a cleaved single-crystal surface plotted on a very expanded vertical scale. Strong electron emission begins near 58 eV, the  $\text{Li}^+$  threshold in the crystal.

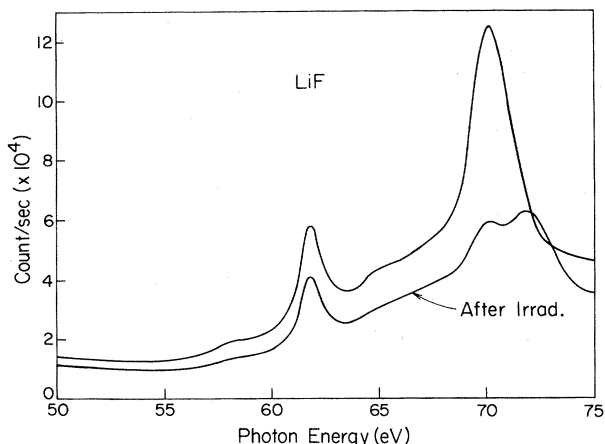


FIG. 4. Electron yield (10 eV) from a LiF surface before and after irradiation with zero-order light for 3 min.

monochromator. The conditions were such that charging occurred, however, the spectral features shown were stable and reproducible. They did not shift in energy with charging nor with electron kinetic energy. The vertical scale in Fig. 3 is greatly expanded and it can be seen that the yield of electrons from this single-crystal surface turns sharply upward at 58 eV. We suggest that 58 eV is the actual threshold corresponding to transitions from the  $\text{Li}^+$   $K$ -shell to excited states in the perfect crystal. The small very narrow peak at 50.8 eV in Fig. 3 was seen using the TGM monochromator under high incident light conditions. Again it probably relates to defects generated by light in the crystal, and as such it will be discussed in the next section.

The grasshopper monochromator could be tuned to zero order at which point the overall undispersed photon flux increased three or four orders of magnitude. Figure 4 shows the electron yield (un-normalized) versus photon energy before (upper curve) and after (lower) a 3-min exposure to zero-order light. The electron energy analyzer was set to 10 eV, therefore one sees an increase in secondary electrons corresponding to the absorption edge around 61.9 eV (data of Fig. 2) and also the strong elastic peak due to the  $\text{Li}^+$  core at 70 eV. Notice that the yield overall has decreased following exposure, but the elastic peak is most strongly affected. In fact, it is split into two, the original peak at 70 eV and a second peak at 71.8 eV. It appears that the initial  $K$ -shell binding energy for a fraction of the lithium has been shifted to lower energy probably due to defects associated with radiation damage. These effects will be discussed toward the end of the next section.

#### IV. DISCUSSION

Let us first consider features of the absorption edge shown in Fig. 2. In the upper part of the figure we indicate transition energies to the four bound states [the states are indicated using standard Boukaert-Smuloukowski-Wigner (BSW) notation] calculated by Kunz, Boisvert, and Woodruff.<sup>9</sup> These authors have used unrestricted

Hartree-Fock theory for the ground and excited states of lithium in a cluster of ions in the LiF crystal. Multiplet splitting is included, so that singlet and triplet final states are calculated taking proper account of electron core-hole exchange interaction (as well as correlation). This is a first-principles calculation without adjustable parameters. For example, the main line at 61.9 eV is due to allowed transition from the  $^1\Gamma_1$  ground state of the system to the singlet  $^1\Gamma_{15}$  excited state ( $1s^2$  to  $1s2p^1P$ ). There is little doubt about the assignment here although the experimental line (61.9 eV) is 0.6 eV below the calculated  $^1\Gamma_{15}$  energy (62.5 eV). Part of this discrepancy is due to the fact that the measurement was made on a film at room temperature. The low-temperature spectrum shifts slightly to higher energy upon cooling.<sup>6</sup>

Likewise by comparing experiment and theory it seems reasonable to assign the observed 58-eV band to the  $^3\Gamma_1$  final state. The singlet-triplet transitions are apparently not seen separately in the free ion, however, Charlotte Moore<sup>18</sup> lists the  $^3S$  and  $^1S$ , in reasonable agreement with the above, and comments that the observed long series should give reliable positions. The dipole operator does not directly couple to the  $^3S$  state, but it may be that magnetic interactions with the surrounding enhance the transition in the solid.

Also shown in Fig. 2, by shading, is the threshold energy for excitation into the continuum, 64.0 eV. This value follows according to Pantiledes and Brown<sup>19</sup> by just adding the 49.5-eV Li- $K$  binding energy relative to the valence-band maximum (refer to Fig. 1) to an upgraded band-gap energy of 14.5 eV.<sup>20</sup> The result agrees quite well with the ionization limit calculated by Kunz, Boisvert, and Woodruff of 63.5 eV.<sup>9</sup> Now it can be seen that the allowed  $^1\Gamma_{15}$  core exciton at 61.9 eV has a binding energy of 2.1 eV. The triplet  $^3\Gamma_1$  core-exciton state (58 eV) has a binding energy of 6 eV. Thus both states are quite compact. Somewhat different conclusions about binding energy are reached in Ref. 7. Finally the shoulder at 60.8 eV can be assigned to  $^1\Gamma_1$  as discussed by Fields, Gibbons, and Schnatterly<sup>7</sup> and/or to the  $^3\Gamma_{15}$  as suggested by Kunz, Boisvert, and Woodruff.<sup>9</sup>

A slight asymmetry appears on the main band indicating underlying absorption beginning about 63 eV. Considering the close proximity of the continuum (64 eV) this is almost certainly due to  $n=2$  and higher allowed exciton states which might be amenable to an effective mass theory with corrections. Such an approximation, of course, is totally inadequate for the  $n=1$   $^1\Gamma_{15}$  and lower-lying states which are very compact. The shoulder, seen to begin in Fig. 2 at 64 eV, is likely due to conduction-band density of states rising from the  $k=0$  minimum.

The great strength of the  $\Gamma_{15}$  exciton is no doubt associated with the compact nature of this final state strongly overlapping the lithium core. It should be kept in mind, however, that the  $\text{Li}^+$  ion is surrounded by a cage of six  $\text{F}^-$  ions so that an "inner-well" effective potential probably contributes to localization and a high oscillator strength.<sup>21</sup>

In Fig. 2 it can be seen that the half width of the main core-exciton band is about 1 eV. This is large but the same order of magnitude as the width of the usual band-

gap exciton in alkali halides. It is due to strong electron-lattice interaction and the oscillating electric fields at the site of the  $\text{Li}^+$  ion in the crystal. According to Toyozawa<sup>22</sup> an x-ray exciton should be Gaussian-type shape. It is difficult to test this in the present case.

Finally, it is worth speculating on the effects of radiation as introduced in connection with Figs. 3 and 4. Lord and Gallon<sup>15</sup> irradiated LiF crystals (300 K) cleaved in UHV with a defocused beam of 900-eV electrons (the dosage was not unlike that used with zero-order light in the present experiment). Following exposure, optical absorption data were then taken in the range 200 to 600 nm (see Fig. 5 of Ref. 15). Absorption bands due to *F*, *M*, and *R* centers were readily observed. All of these negative-ion vacancy centers will perturb nearby exciton transitions. Since the *R* bands were especially strong it is worth considering this defect in connection with both the splitting of the 70-eV elastic peak (Fig. 4) and the narrow line shown in Fig. 3.

The well-accepted model for the *R* center is an aggregate of three neighboring *F* centers forming an equilateral triangle in the (111) plane. The defect has  $C_{3v}$  symmetry and one nearby  $\text{Li}^+$  ion is close [probably drawn in toward the (111) plane containing the three vacancies plus electrons].<sup>23</sup> The *R* absorption bands in LiF show especially strong zero-phonon lines at their low-energy edges.<sup>24</sup> The  $\text{Li}^+$  core electrons might be viewed as part of the *R*-center defect, therefore we suggest that the narrow line seen at 50.7 eV in Fig. 3 is a zero phonon transition from the  $\text{Li}^+$  core to an accessible excited state of the

defect. Here the observed linewidth is comparable to our instrument resolution, 0.1 eV. This feature should be studied with higher resolution and at low temperature.

If the narrow 50.8-eV line is due to a transition from the  $\text{Li}^+$  core in a defect center, Fig. 1 suggests that the final state lies 1.3 V above the top of the valence band. This excited state of  $\text{Li}^+$  is likely shifted below the usual core-exciton transitions by a combination of initial-state binding-energy shift (see Fig. 4) and final-state Madelung potential associated with the reduced coordinates and electron distribution within the defect. Obviously further experimental and theoretical investigation is called for.

#### ACKNOWLEDGMENTS

The authors would like to thank A. B. Kunz, J. C. Boisvert, and T. O. Woodruff for communicating their theoretical results prior to publication. They would also like to thank Ward Plummer for use of his monochromator and beam line during part of the investigations. Also discussions with C. Olson were very helpful. The cooperation and support of the staff of the University of Wisconsin Synchrotron Radiation Center is much appreciated. This facility was supported by the National Science Foundation Grant No. NSF DMR 80-20164. At the University of Illinois the research was supported by a grant to the Physics Department, Grant No. NSF-DMR 82-13068 and to the Materials Research Laboratory Grant No. NSF-DMR 80-20250 for facilities development.

\*Now at Synchrotron Radiation Center, 3725 Schneider Dr., Stoughton, WI 53589.

†Now at Physics Department, Brookhaven National Lab., Upton, NY 11973.

‡Now at Physics Department, University of Notre Dame, Notre Dame, IN 46556.

<sup>1</sup>A. P. Lukirskii, O. A. Ershov, T. M. Zimkina, and E. P. Savinov, *Fiz. Tverd. Tela (Leningrad)* **8**, 1787 (1966) [*Sov. Phys. Solid State* **8**, 1422 (1966)].

<sup>2</sup>F. C. Brown, C. Gahwiller, A. B. Kunz, and N. O. Lipari, *Phys. Rev. Lett.* **25**, 262 (1970).

<sup>3</sup>B. F. Sonntag, *Phys. Rev. B* **9**, 3601 (1974).

<sup>4</sup>W. Gudat, C. Kunz, and H. Petersen, *Phys. Rev. Lett.* **32**, 1370 (1974).

<sup>5</sup>E. T. Arakawa and M. W. Williams, *Phys. Rev. Lett.* **36**, 333 (1976).

<sup>6</sup>C. G. Olson and D. W. Lynch, *Solid State Commun.* **31**, 51 (1979).

<sup>7</sup>J. R. Fields, P. C. Gibbons, and S. E. Schnatterly, *Phys. Rev. Lett.* **38**, 430 (1977).

<sup>8</sup>A. Zunger and A. J. Freeman, *Phys. Lett.* **A60**, 456 (1977); *Phys. Rev. B* **16**, 2901 (1977).

<sup>9</sup>A. B. Kunz, J. C. Boisvert, and T. O. Woodruff, preceding pa-

per, *Phys. Rev. B* **29**, 2158 (1984).

<sup>10</sup>B. P. Tonner, *Nucl. Instrum. Methods* **172**, 133 (1980).

<sup>11</sup>F. C. Brown, R. Z. Bachrach, and N. Lien, *Nucl. Instrum. Methods* **152**, 73 (1978).

<sup>12</sup>F. T. Himpfel and W. Steinmann, *Phys. Rev. B* **17**, 2537 (1978).

<sup>13</sup>W. Pong and C. S. Inouye, *J. Electron Spectrosc. Relat. Phenom.* **11**, 165 (1977).

<sup>14</sup>A. B. Kunz, *Phys. Rev. B* **26**, 2056 (1982).

<sup>15</sup>D. G. Lord and T. E. Gallon, *Surf. Sci.* **36**, 606 (1973).

<sup>16</sup>R. Haensel, C. Kunz, T. Sasaki, and B. Sonntag, *Appl. Opt.* **7**, 304 (1968).

<sup>17</sup>W. Gudat and C. Kunz, *Phys. Rev. Lett.* **29**, 169 (1972).

<sup>18</sup>C. E. Moore, National Bureau of Standards Report No. 467, 1948 (unpublished).

<sup>19</sup>S. Pantelides and F. C. Brown, *Phys. Rev. Lett.* **33**, 298 (1974).

<sup>20</sup>M. Piacentini, *Solid State Commun.* **17**, 697 (1975).

<sup>21</sup>T. Aberg and J. L. Dehmer, *J. Phys. C* **6**, 1450 (1973).

<sup>22</sup>Y. Toyozawa, *Prog. Theor. Phys.* **20**, 53 (1958).

<sup>23</sup>W. B. Fowler, *Physics of Color Centers* (Academic, New York, 1968), p. 577, see Figs. 8–10.

<sup>24</sup>R. H. Silsbee, *Phys. Rev.* **138A**, 180 (1965).