Band Dispersion of Localized Valence States in LiF(100)

F. J. Himpsel, L. J. Terminello,[a] D. A. Lapiano-Smith, E. A. Eklund, and J. J. Barton

IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 11 March 1992)

The band dispersion of the localized, F $2p$-like valence band of LiF is mapped using an imaging technique to obtain $k(E)$. The bandwidth is 3.5 eV (from Γ_{15} to X'_4). This is 17% wider than predicted by first-principles band calculations, implying an expansion of the bandwidth by self-energy effects in qualitative agreement with quasiparticle calculations. The self-energy effect is opposite to that seen in delocalized systems, such as alkali metals.

PACS numbers: 71.25.Tn, 79.60.Eq

The electronic structure of highly correlated, localized systems is experiencing a renaissance with the advent of high-temperature superconductivity and powerful computational techniques to handle electronic states that are neither completely delocalized (bandlike) nor completely localized (such as core levels). The most basic characteristic of these states is their bandwidth. Its value relative to the Coulomb-exchange energy determines the degree of correlation. The bandwidth has been taken [1-3] as a crucial measure of self-energy effects in testing quasiparticle calculations, which represent the state of the art in band theory. The $3d$ and $4f,5f$ systems typically associated with highly correlated states are rather complex, even in simple crystal structures [4], let alone in the multilayered perovskite structures of high-temperature superconductors. Therefore, it is useful to search for simpler prototype materials containing p or s electrons, preferably with low atomic number. We have chosen the F $2p$ valence band of LiF as a model system. It may be considered the deepest valence band of any solid because LiF has the largest band gap [5] of ordinary materials (with the exception of exotic solids, such as rare gases).

Recently we have found a way to grow LiF(100) epitaxially on Ge(100) with bulklike crystal quality [6]. This avoids many broadening effects, such as charging, small crystallite size, and inhomogeneous Fermi-level pinning, which have hampered previous attempts to obtain bandwidths of alkali halides [7-11]. Using angle-resolved photoemission we are able to accurately determine the dispersion and width of the F $2p$ band in LiF. Our width of 3.5 eV is 17% larger than predicted by first-principles, ground-state band calculations, which shows that self-energy effects play a role in determining the bandwidth. This agrees qualitatively with the 10% bandwidth increase calculated for LiCl in state-of-the-art quasiparticle calculations. Interestingly, the sign of the self-energy effect is opposite to that for free-electron-like materials, again in agreement with quasiparticle calculations.

The band mapping method used here differs from the usual approach of taking angle-resolved photoelectron spectra. Instead of determining the energy distribution of photoelectrons at fixed momentum we obtain the momentum distribution at fixed energy using a display spectrometer [12,13]. Reversing the two variables helps for nar-
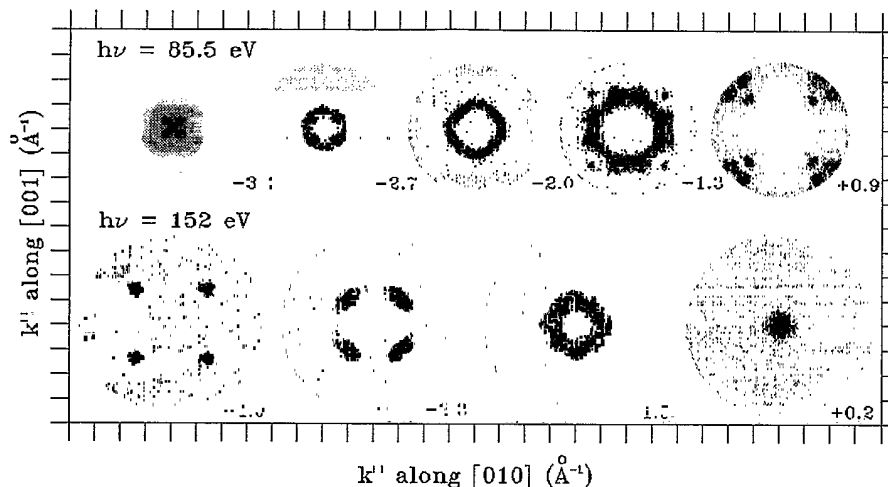

FIG. 1. Momentum distributions of photoelectrons from the F $2p$ valence band of LiF(100) at various electron energies relative to the valence-band maximum. The two photon energies are chosen such that the valence-band maximum (Γ_{15}) and minimum (X'_4) appear in normal emission, respectively. The pictures are centered around the surface normal. Areas of high emission intensity appear dark.

row bands since we get a large momentum change for a small energy difference. Such momentum distributions are shown in Fig. 1 for two photon energies and a series of electron energies across the F $2p$ valence band of LiF. The raw data have been normalized to the analyzer transmission (determined from secondary electrons), converted to a momentum scale linear in $k^{\parallel}$ by ray tracing, and fourfold averaged according to the symmetry of the LiF(100) surface. All the structures discussed here were clearly visible in the raw data.

In order to map the band structure along high symmetry directions we have chosen photon energies such that the final-state energy surface nearly coincides with planes equivalent to the (100) plane in k space (Fig. 2). The two photon energies $h\nu = 88.5$ and 152 eV have been adjusted such that this coincidence is exact at $k^{\parallel}=0$. Essentially, the photon energy was fine tuned until a single spot was seen in normal emission at the valence-band maximum for $h\nu = 152$ eV and at the valence-band minimum for $h\nu = 88.5$ eV. Going away from the optimum photon energy caused the single spot to split into four, corresponding to a slice through the valence band away from its extremal points. Because of the curvature of the free-electron-like final energy surfaces (see Fig. 2) there is a drift away from the high symmetry planes at finite $k^{\parallel}$. That could in principle be corrected by retuning the photon energy, such that the next conduction-band minima or maxima at $k^{\parallel}=(011)2\pi/a$ become single spots. For example, the picture at $h\nu = 88.5$ eV and $+0.9$ eV relative to the valence-band maximum has the spots split into triplets (the fourth component being just outside the field of view), because of transitions slightly off the high symmetry plane. These would merge into single spots when increasing the photon energy. For simplicity we have avoided readjusting the photon energy, but have chosen two photon energies such that one of them ($h\nu = 152$ eV) gives exact results near Γ, the other ($h\nu = 88.5$ eV) near X. Thus we obtain our most accurate results near the valence-band maximum and minimum, respectively. For most of the intermediate energies the two dispersion curves overlap well (open and solid circles in Fig. 3), and only at the other extremal
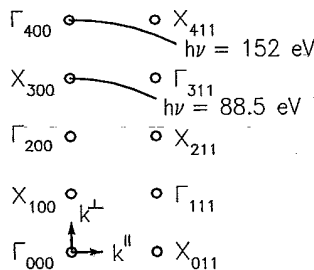
point $k^{\parallel}=(110)$ they deviate from the exact result at $k^{\parallel}=(000)$. These points have been omitted from Fig. 3. The pictures allow us to determine momenta in the whole (100) plane, but we focus on the (011) azimuth, which exhibits the strongest emission features. It probes the $\Gamma\Sigma KSX$ line in momentum space, and thus covers the valence-band maximum Γ_{15} as well as the valence-band minimum X'_4. The (010) azimuth would give the $\Gamma\Delta X$ line.

Figure 3 shows the experimental band dispersion obtained from the strongest emission maxima in Fig. 1. A sinusoidal interpolation curve is provided as a guide to the eye and as a measure of the bandwidth. Its full width is 3.5 eV. Band calculations [14–17] show that the six F $2p$ states give rise to three bands (Σ_1, Σ_3, Σ_4) along the [011] direction, with the Σ_1 and Σ_4 bands converging onto the upper X point (X'_5), while only the Σ_3 band spans the full width of the valence band down to X'_4. Comparing the band topology with our data we conclude that the Σ_3 band corresponds to the strongest emission peak that is plotted in Fig. 3.

The key parameters characterizing the band structure of LiF are the band gap (14.1–14.5 eV [5]) and the width of the valence band (3.5 eV from our work). Valence bandwidths of 3.35–3.7 eV [8] have been obtained from the full width of half maximum of angle-integrated valence-band spectra. These values go up to 6.1 eV [8] when using the full width at the peak base, showing that a great deal of uncertainty is involved when trying to determine the bandwidth from the width of the photoelectron spectrum. Comparing our own angle-integrated spectra with the band dispersion measurement points towards the same problems (see Fig. 3). Angle-integrated valence-band spectra are broadened by various

FIG. 2. Location of the transitions along the [011] azimuth in Fig. 1. The unit in k space is $2\pi/a = 1.56$ Å^{-1}.
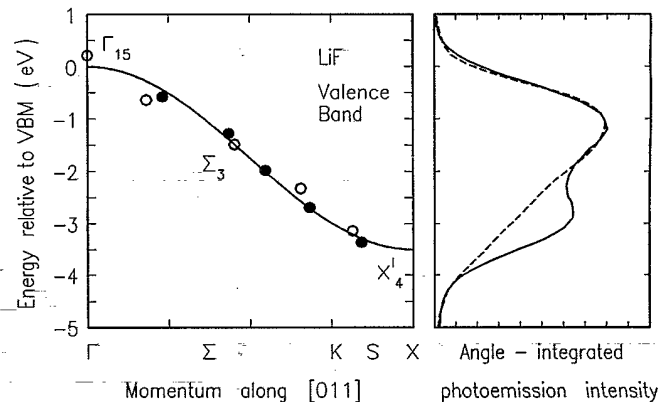
FIG. 3. Band dispersion of the prominent features in Fig. 1 along the [011] azimuth. A sinusoidal line interpolates the data points, giving a bandwidth of 3.5 eV. Solid circles are obtained at $h\nu = 88.5$ eV; open circles at $h\nu = 152$ eV. Energies are referenced to the valence-band maximum (VBM). For comparison, angle-integrated energy distribution curves are shown for $h\nu = 86$ eV (dashed) and $h\nu = 125$ eV (solid).

effects, e.g., charging, phonons, inhomogeneous Fermi-level pinning, and small crystallite size in polycrystalline films. Even for our high-quality epitaxial films, where these effects are minimized, the full width of the angle-integrated valence-band spectra in Fig. 3 is larger than the actual bandwidth obtained from the dispersion measurement. When looking in the tails of the spectrum at the photoelectron angular distribution we find it unchanged from that at the band edge, indicating that the tails are due to broadening.

When comparing the experimental band structures with calculations one has to keep in mind that, strictly speaking, only quasiparticle calculations provide a valid description of the photoemission experiment by including the self-energy of a hole in the valence band. Such calculations have recently become feasible for alkali halides, such as LiCl [17]. Ground-state energy eigenvalues obtained from Hartree-Fock or local-density calculations in traditional fashion do not represent the states that can be measured, i.e., holes in the valence band and electrons in the conduction band. The artificial nature of such eigenvalues shows up in the fact that they depend on the calculation method. For example, the band gap of LiF comes out too large in Hartree-Fock calculations [15] (22.7 eV) and too small in local-density theory [14] (9.8 eV in a X_α calculation with $\alpha = \frac{2}{3}$), compared to an experimental gap of 14.1–14.5 eV [5]. After including the respective self-energy corrections to the Hartree-Fock and local-density bands they should both coincide with experiment, as they do for semiconductors (see Ref. [17] and references therein). Indeed, applying approximate self-energy corrections of the electronic polaron type to the Hartree-Fock bands [15] gives a gap of 14.0 eV, which is close to the experimental results. Likewise, including excited-state effects in the local-density bands using a Δ-self-consistent-field scheme [14] results in a band gap of 13.9 eV.

While the self-energy correction to the band gap is affected by the switch from holes in the valence band to electrons in the conduction band, the correction to valence bandwidth is more subtle, involving exclusively holes. Our data allow us to focus on this effect, which has not been accessible to an experimental test until now, due to the uncertainties in the bandwidth measurements. Comparing our bandwidth of 3.5 eV with the Hartree-Fock value [15] of 3 eV and the local-density value [14] of 3.0 eV ($\alpha = \frac{2}{3}$), we find an expansion of the valence bandwidth by self-energy effects in both cases. Approximate self-energy corrections to the Hartree-Fock bandwidth [15] give a value of 3.1 eV, still significantly lower than the experiment. The corresponding self-energy correction for the local-density bands of LiF has not been worked out, but there exists a state-of-the-art quasiparticle calculation [14] of the self-energy for LiCl. It shows that the self-energy expands the width of the valence band by 10%. This is in qualitative agreement with the

17% expansion obtained by comparing our data with the local-density ($\alpha = \frac{2}{3}$) calculation [11] for LiF.

The influence of the self-energy on the bandwidth has been discussed mainly in the context of alkali metals, where it has attracted attention [1–3] due to the simplicity of their free-electron-like, delocalized valence band. Our results on LiF represent again a simple system, but at the opposite end of the localization scale, with atomic-like, localized states. It is interesting to see that the self-energy acts in opposite directions in these extreme cases, shrinking the alkali valence band and expanding that of the alkali halide. In the future, our result, and the application of our method to other narrow-band systems, will make it possible to quantify the self-energy effect on the bandwidth in localized systems. The correlation between experiment and theory can then be used to aid in the validation of computational methods for calculating the self-energy of quasiparticles.

(a)Present address: Lawrence Livermore National Laboratory, P.O. Box 808, MS L-268, Livermore, CA 94550.

[1] E. Jensen and E. W. Plummer, Phys. Rev. Lett. **55**, 1912 (1985); In-Whan Lyo and E. W. Plummer, Phys. Rev. Lett. **60**, 1558 (1988).

[2] J. E. Northrup, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **59**, 819 (1987).

[3] K. W.-K. Shung, Bo. E. Sernelius, and G. D. Mahan, Phys. Rev. B **36**, 4499 (1987); K. W.-K. Shung, Phys. Rev. B **44**, 13112 (1991).

[4] F. J. Himpsel, D. E. Eastman, E. E. Koch, and A. R. Williams, Phys. Rev. B **22**, 4604 (1980).

[5] A gap of about 14.5 eV was reported in M. Piacentini, Solid State Commun. **17**, 697 (1975). A gap of 14.2±0.2 eV was found in M. Piacentini, D. W. Lynch, and C. G. Olson, Phys. Rev. B **13**, 5530 (1976). A gap of 14.1±0.1 eV was determined from the onset of photoemission from single-crystal LiF(100) in F. J. Himpsel, Ph.D. thesis, University of Munich, 1976 (unpublished).

[6] D. A. Lapiano-Smith, E. A. Eklund, F. J. Himpsel, and L. J. Terminello, Appl. Phys. Lett. **59**, 2097 (1991).

[7] S. P. Kowalczyk, F. R. McFeely, L. Ley, R. A. Pollak, and D. A. Shirley, Phys. Rev. B **9**, 3573 (1974).

[8] R. T. Poole, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, Phys. Rev. B **11**, 5179 (1975); see Refs. [34,35] in this paper for earlier x-ray photoemission spectroscopy data on the bandwidth of LiF.

[9] F. J. Himpsel and W. Steinmann, Phys. Rev. Lett. **35**, 1025 (1975); Phys. Rev. B **17**, 2537 (1978).

[10] W. Pong, D. Paudyal, and D. Brandt, J. Electron Spectrosc. Relat. Phenom. **21**, 261 (1980).

[11] H. Onuki and T. Saito, J. Phys. Soc. Jpn. **54**, 2797 (1985).

[12] D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, Nucl. Instrum. Methods **172**, 327 (1980).

[13] A. Santoni, L. J. Terminello, F. J. Himpsel, and T. Takahashi, Appl. Phys. A **52**, 299 (1991).

[14] A. Zunger and A. Freeman, Phys. Rev. B **16**, 2901 (1977); see references in this paper for earlier theoretical work on the band structure of LiF.

[15] A. Barry Kunz, Phys. Rev. B **26**, 2056 (1982); see references therein for earlier Hartree-Fock work.

[16] Yan Li, J. B. Krieger, M. R. Norman, and G. J. Iafrate, Phys. Rev. B **44**, 10437 (1991).

[17] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **32**, 7005 (1985); **34**, 5390 (1986); see references therein for earlier self-energy calculations.