Core Exciton and Band Structure in LiF

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Core Exciton and Band Structure in LiF

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By applying yield spectroscopy we could confirm recent absorption measurements localizing the onset of Li^+ 1s transitions at 54 eV. From EDC-measurements using 120 eV photons the Li^+ 1s separation from the top of the valence band is found to be 50.2 eV. Combining these numbers with the band gap width (13.6 eV) we find an electron-hole interaction energy of 10 eV. This is discussed on the background of two recent theoretical calculations of ε_2-spectra.

The optical properties of the widest band gap ionic insulator LiF have been the subject of extensive experimental and theoretical investigations. Very recently two calculations of the Li^+ 1s absorption in LiF by Menzel et al.[1] and A.B. Kunz et al.[2] were published. Including the earlier work of A.B. Kunz et al.[3] there are altogether three different approaches based on solid-state theory trying to interpret the core electron spectrum of LiF, or, more generally speaking of insulators:

(1) pure bandstructure,

(2) bandstructure with excitons as additional structures below conduction band critical points,

(3) bandstructure with a conduction band rigidly shifted towards the valence band because of the electron hole attraction.

In approach (1) which is used in the paper by Menzel et al.[1] the importance of the electron hole interaction is denied. These authors compute Hartree Fock Slater self consistent field (SCF) bands and calculate ε_2 the imaginary part of the dielectric constant including matrix elements. Their spectrum shows the onset of Li^+ 1s transitions at about 55 eV (Fig. 1). The dominant peak is obtained near (deviation $\Delta E \sim 2$ eV) to the corresponding one found in the experiments[4,5] and is of similar shape.

Approach (2) is suggested e.g. in Ref. 3. It is based on comparing the positions of critical points with structures in the experimental curve.

Approach (3) is based on a rigorous Hartree-Fock SCF band structure calculation from which A.B. Kunz et al.[2] calculated ε_2 with the inclusion of matrix elements. Their ab initio result places the onset of the Li^+ 1s transitions

at about 73 eV. Corrections due to electron and hole polarization of the environment shift the whole spectrum rigidly down by 10 eV. Finally the effect of the local hole in the 1s level on the excited electron in the conduction band is estimated from atomic term values of Li^+ and Li^{++} to be another 10 eV. The authors use this value to perform another rigid shift of the spectrum yielding a final onset at 53 eV. They are aware of the crude nature of these corrections, nevertheless the most prominent peak comes to lie near to the experimental one ($\Delta E \sim 3$ eV, see Fig. 1). In agreement with the spectrum of Menzel et al.[1] weak structure due to transitions into the lowest s-type part of the conduction band shows up in the region from the onset at 53 eV to 60 eV. At that time no such structure was observed experimentally. In a careful reinvestigation of the optical absorption of LiF Sonntag[6] recently found a weak absorption band with its onset around 53 to 54 eV which is identified with these transitions.

We report here on photoelectric measurements giving an independent check on this weak band by the method of yield spectroscopy[7]. Moreover we have measured energy distribution curves (EDC) of photoemitted electrons which give the accurate position of the valence band relative to the Li^+ 1s band. Combining this with the Li^+ 1s absorption spectrum (resp. yield) and the valence band absorption spectrum[8,9] we are able to establish the magnitude of the electron hole interaction from an experimental point of view.

The measurements were performed in an UHV-system at a base pressure in the 10^{-10} Torr range. The samples were prepared in situ by evaporation from tungsten boats onto conducting substrates. During evaporation the pressure rose to the upper 10^{-9} Torr range.

The photoelectric yield was measured as a function of photon energy ("yield spectroscopy") under an angle of incidence of 45° using a gold reference standard. Synchrotron radiation was monochromatized in the energy range 20 - 180 eV with a spectral resolution E/ΔE of about 400, e.g. 0.3 eV at 120 eV photonenergy. EDC curves were obtained with an angle of incidence of the light of 70° in s-polarization. We used a spherical electrostatic analyzer having a typical energy resolution of 0.4 eV. Positive charging of the specimen can result in a shift and in broadening of EDC structures. Therefore we have used very thin samples ($\sim$100 Å) for EDC measurements. This is justified because of the extremely short inelastic scattering length (5 - 20 Å) of electrons with kinetic energies above 20 eV. Further details will be given elsewhere.

In the upper part of Fig. 1 we show the photoelectric yield spectrum of LiF. It is not corrected for reflectance and the distortions due to the gold standard which cannot, however, account for any of the observed structures. Taking a proper extrapolation of the tail of the valence band plus the F^-2s transitions the onset of additional absorption due to the Li^+1s transitions begins at about 54 eV. At 56.5 and 58.3 eV weak structures show up which are not as prominent in Sonntag's[6] absorption spectrum. This can be verified from a direct comparison in Fig. 1. We attribute this to the better statistical accuracy inherent in yield spectroscopy. The rest of the spectrum is in very good agreement with Sonntag's[6] and also with earlier absorption measurements[4,5]. Especially noteworthy is the prominent peak at 61.9 eV with its two characteristic sidebands which show up clearly in the yield spectrum. This peak relates to the one derived from the p-type bands in the two theoretical curves. If we shifted these p-type bands down in energy by $\sim$2 eV (resp. $\sim$3 eV), the 54 to 64 eV part of the experimental spectrum would be in surprisingly good agreement with both theoretical curves especially with the result of Menzel et al.[1]

In Fig. 2 we show the result of our EDC measurement[10] It is well known to be
somewhat difficult to refer binding energies of insulators to the Fermi level.
Therefore we give the energies relative to the top of the valence band (VB).
120 eV photons are capable of exciting all valence and core electrons with the
exception of F^-1s ($\sim$686 eV). We find a valence band density of states with two
maxima at an energy separation of 2.0 eV and a valence band half width of
3.5 eV. The F^-2s band is located at -23.7 eV, the Li^+1s level at -50.2 eV. The
latter has a half width of 1.4 eV, which is apparently more than the overall
experimental resolution of 0.5 eV. There is a lot of other structure arising
from secondary processes like electron-electron scattering, plasmon excita-
tions and Auger electrons (CEL and Aug resp.). We have indicated some of these
structures in Fig. 2. A full discussion will be given elsewhere.

Using the information given in Figs. 1 and 2 as well as the results in the fun-
damental absorption region[8,9] we have constructed a schematic energy level
diagram based on a one electron picture in order to reveal the discrepancies
expected due to the electron hole interaction. The valence band spectrum[9] is
given in the left part of Fig. 3, the Li^+1s spectrum in the right part. The
energy difference of valence and Li^+1s bands as measured in the EDC spectrum
is used to localize the two spectra relative to each other. We realize that
there is a separation of 8 eV between the onsets of valence and core band tran-
sitions in such a representation. In the remainder of this letter we shall
analyze the consequences of this separation.

The onset of the Li^+1s absorption at an energy 8 eV below that of the valence
band absorption means a complete breakdown of the pure band picture (approach
(1))[11]. The only possibility is to interprete it as an effect of the electron-
hole interaction. Following A.B. Kunz et al.[2] we argue that the electron in the

conduction band has a much stronger interaction with the well localized hole
in the Li^+1s state than with the less localized hole in the valence band. The
difference in localization has to account for the 8 eV difference in binding
energy.

If we assume approach (2) (classical excitons) to be the correct explanation
of the fundamental absorption spectrum as it is usually done (Ref. 3,8,9)
we have to place the bottom of the conduction band at 13.6 eV[9]. Using the
same level according to Fig. 3 for the Li^+1s spectrum we have to attribute
the weak absorption band between 54 and 60 eV to a s - s forbidden exciton
band and the dominant structure centered at 61.9 eV to a s - p allowed exciton
band. This implies that we have to place the onset of interband transitions
at 63.8 eV which is just the energy of the pronounced minimum in the absorption
spectrum. But furthermore it implies exciton binding energies of 10 eV.

A certain agreement is obtained also by applying approach (3). Here the elec-
tron hole interaction (10 eV) is taken into account, but only by rigidly
shifting the initial spectrum derived from the ab initio band calculation.
However, the procedure is conceptually unsatisfactory. The shifted states
have to be localized in a Coulomb potential well of the size less than one
unit cell while originally they have been calculated for an infinite periodic
crystal.

In this context it is interesting to note that the equation of Ref. 2 which
was used to determine the Coulomb attraction of the Li^+1s hole on the excited
electron gives an energy of 13 eV with the data of Ref. 12. This would give
rise to a nearly complete agreement of the position of the dominant peak with
experiment. In accordance with A.B. Kunz et al., however, we argue that the
similarity in the shape of the spectra must be considered to be accidental.

We have to stress on the other hand that the energy values of this calculation together with measurements like ours are extremely important. Since this band calculation is an <u>ab initio</u> SCF calculation treating exchange properly, any deviation between the theoretical and experimental energy values can be traced back to the polarization of the environment and electron-hole interaction. Since the polarization effects can be estimated properly[2], we have available an absorption spectrum obtained from a correlation corrected one electron band calculation of LiF. Defining excitonic effects as the deviations of experimental results from the results of such a band calculation we are able to state that we have found indeed very large excitonic shifts (10 eV!).

It has been shown that the electron-hole interaction cannot be considered to be a weak perturbation for core excitations in insulators like LiF. We believe that further progress in calculating core absorption spectra could start from atomic and molecular theory rather than band calculations. In order to stress this point we show the long noted coincidence between the lowest excited levels[12] of the Li^+ free ion and the LiF excitations in Fig. 1.

References and Footnotes

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9. G. Stephan, thesis (University of Rennes, unpublished, 1970)

10. ESCA data are available for LiF.

   a) K. Hamrin, G. Johansson, U. Gelius, C. Nordling, and K. Siegbahn, Physica Scripta $\underline{1}$, 277 (1970)

   b) C.K. Jørgensen and H. Berthou, Det Kongelige Danske Videnskabernes Selskab Matematisk-fysiske Meddelser $\underline{38}$, 15 (1972)

   But according to Hamrin et al. the binding energy of the Li^+ 1s level is not reliable due to heat treatment of the specimen. Jørgensen and Berthou have used powdered samples. They only give the energies of the maxima, whereas we are interested in the onset of the valence band.

11. It is possible, in principle, to ascribe the weak structures in the range 54 to 60 eV to F^- 2s or valence band transitions. Usually, however, such structures far above threshold are much broader. Moreover the fact that we would then find a very prominent peak at the onset would not agree with the general expectation that the lowest excited states are of the forbidden s – s type.

12. C.E. Moore, Natl.Bur.Stand. (U.S.) Circ. No. 467 Vol. I (1949)

Figure Captions

Fig. 1   The experimental photoelectric yield (fat solid) spectrum of this

work is compared with Sonntag's experimental absorption result

(thin solid) and the calculated ε_2-spectra of Menzel et al. (dashed)

and of A.B. Kunz et al. (dash-dotted). The vertical bars give the

energy position of transitions in Li^+ ions according to the tabu-

lated data of Moore.

Fig. 2   Electron energy distribution curve of a thin film of LiF.

Symbols are explained in the text.

Fig. 3   Data of optical and electron spectroscopy are composed to reveal the

effect of the electron hole interaction. The zero of the energy scale

on the left side is chosen in a such a way that it gives the photon

energy of the fundamental absorption spectrum (top left), the energy

scale on the right side gives the photon energy of the Li^+ ls core
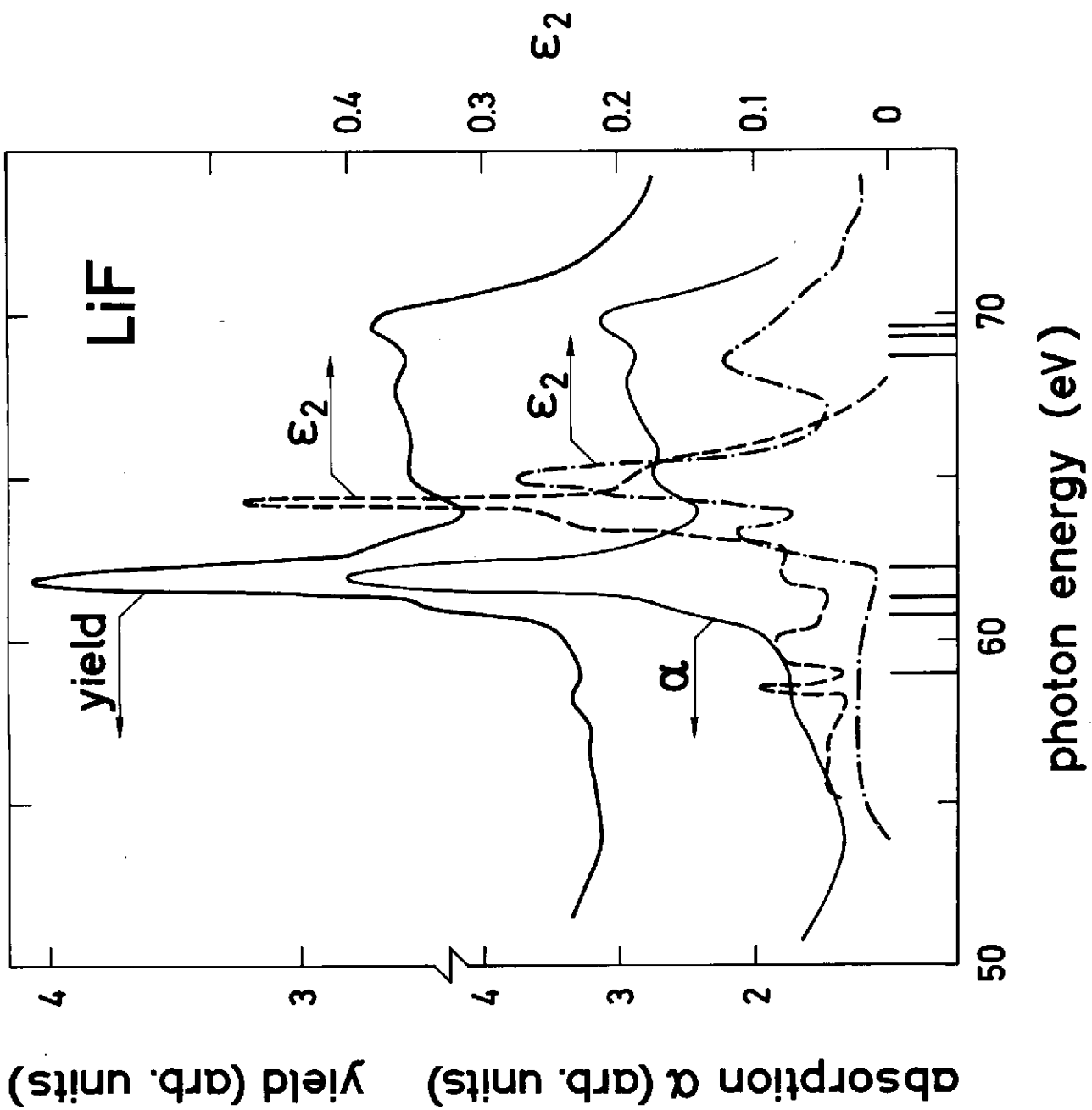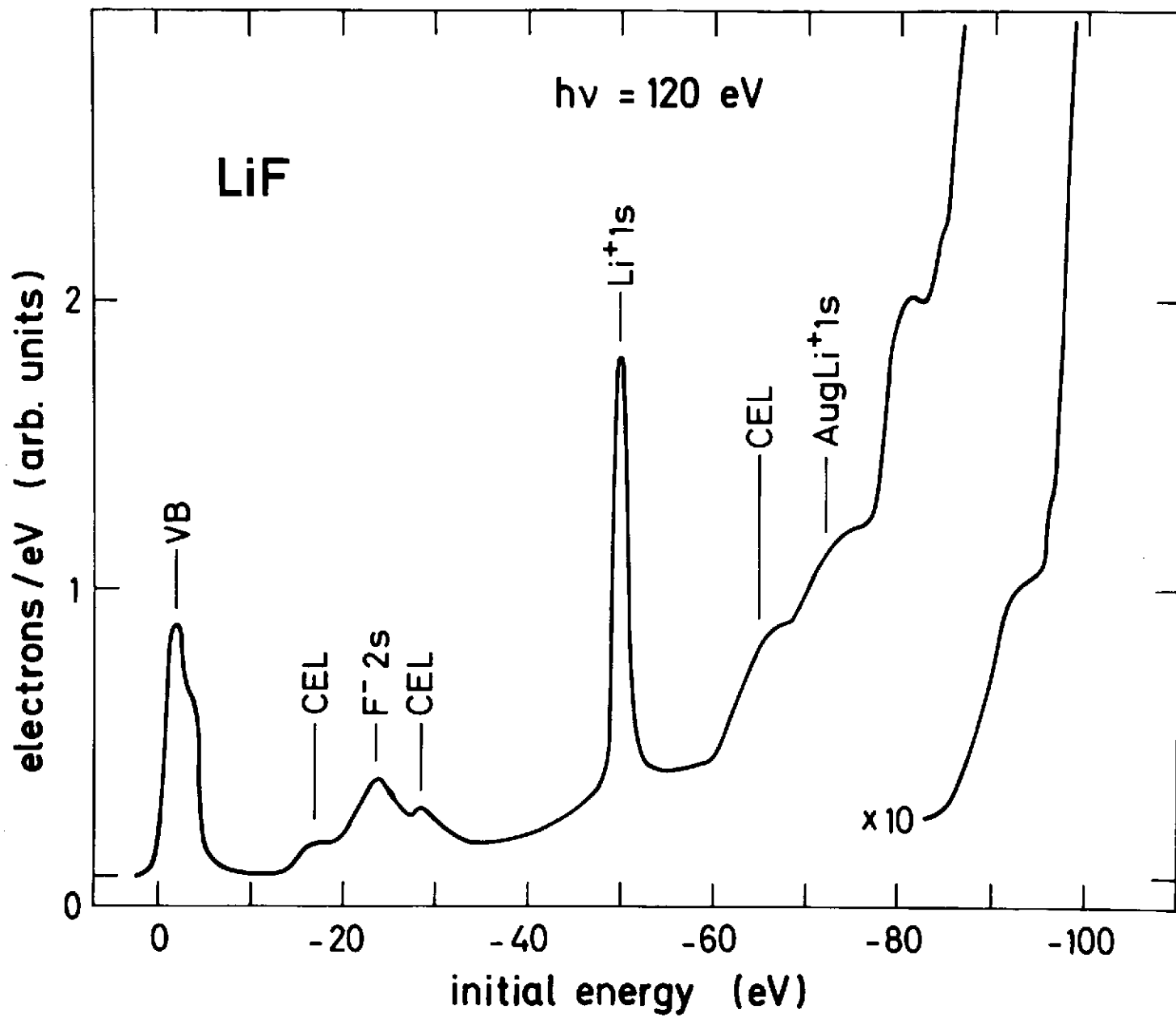
absorption in LiF (top right).

Fig. 1

Fig. 2

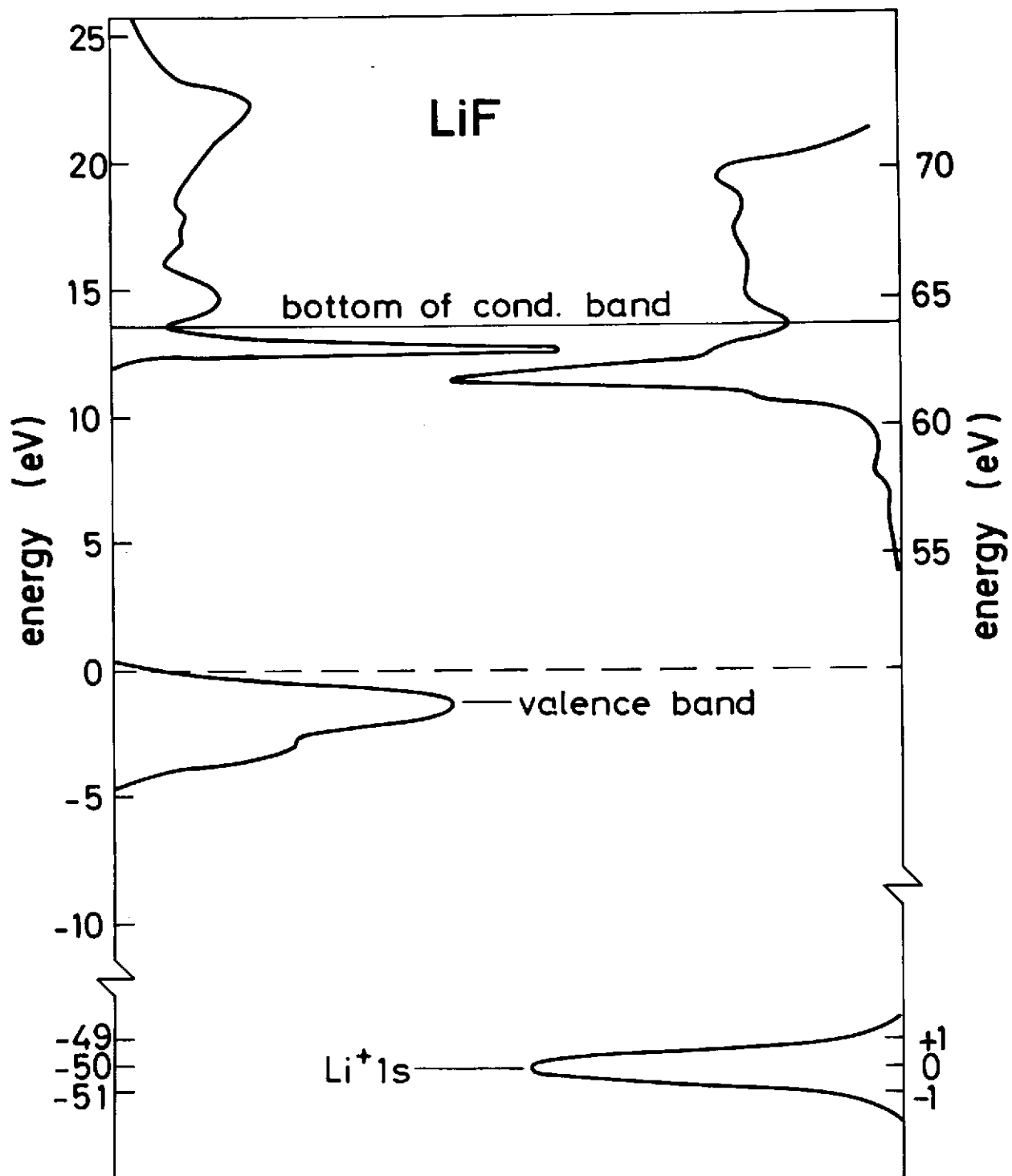Fig. 3