Observations of "forbidden" soft-x-ray transitions: Li K absorption in LiF†

B. F. Sonntag*
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 5 November 1973)

A weak absorption band at 53.5–60 eV, associated with transitions from the Li 1s core level to the s-like conduction band of LiF, has been detected, confirming the results of recent band calculations.

Transitions from the Li K (1s) shell to the predominantly s-symmetric conduction-band states of LiF are parity forbidden at $k=0$ and only weakly allowed throughout the rest of the Brillouin zone and therefore should give rise only to a weak absorption. Recent calculations of the Li K-absorption spectrum of LiF, based on self-consistent bands, by Menzel *et al.*[1] and by Kunz *et al.*[2] predict a weak absorption band due to these transitions, which extends from approximately 54 up to 62 eV. Allowed transitions of Li 1s electrons to conduction-band states lying more than 8 eV above the conduction-band minimum, which have predominant Li 2p character, show up as a strong maximum at 64 eV in both calculated spectra. The dominant absorption maximum at 61.9 eV found experimentally[3,4] has been identified with these transitions by Menzel *et al.* and by Kunz *et al.* The experimental results published so far[3,4] have not been extended far enough below 60 eV to allow one to decide whether the small absorption at lower energies predicted by the theory is there or not.

The absorption of LiF was determined in the energy range from 50 to 72 eV by observing the transmission of thin films (thickness between 200 and 1000 Å) evaporated *in situ* onto aluminum substrates cooled to liquid-nitrogen temperature. The samples, surrounded by a liquid-nitrogen cold trap to prevent contamination in the 10^{-6}-Torr vacuum, were irradiated by the synchrotron continuum of the University of Wisconsin Physical Sciences Laboratory 250-MeV electron storage ring. The energy resolution of the 2-m grazing-incidence Rowland-type spectrometer (slit width 10 μm, grazing angle of incidence 4°, 576-lines/mm grating) in the energy range covered by these measurements was better than 0.1 eV. Details of the experimental arrangement and procedure are given elsewhere.[5]

Figure 1 shows the experimental results. At approximately 53.5 eV, we find the onset of a weak absorption due to transitions from the Li 1s level. Because of the background originating from valence-band transitions, the absorption threshold could not be located more precisely. With increasing photon energy, the Li 1s absorption rises slowly towards a small maximum at 58 eV. The strong maximum at 61.9 eV and the structures found at higher energies are in good agreement with previous results.[3,4] Since the refractive index n is approximately unity in the soft-x-ray region, the absorption coefficient α can be easily converted to the imaginary part of the dielectric constant ϵ_2 ($\epsilon_2 = nc\alpha/\omega$). In these measurements, only the relative spectral behavior of α was determined, thus the ϵ_2 spectrum shown in Fig. 2 was obtained using the absolute value for α at the peak given by Brown *et al.*[4] The error in ϵ_2 is estimated to be ~50%, but the error in the relative values is less than 10%. For comparison, the theoretical ϵ_2 spectra are included in Fig. 2.

The experimental results establish the existence of the low-absorption band between 53.5 and 60 eV, which has been predicted by both calculations. The prominent maximum at 61.9 eV in the experimental spectrum lies 2 eV below its counterpart at 64 eV in the theoretical curves. This indicates that the distance between the conduction-band minimum and the dominant p-like states is 2 eV smaller than found theoretically. Shifting the spectra in such a way that the strong maxima line up does not result in a one-to-one correspondence of the structures found in the theoretical spectra and the experimental spectrum. For example, the strong absorption found experimentally at ~70 eV is not accounted for by the theoretical spectra based on band-to-band transitions. Kunz *et al.*[6] suggested that this ab-

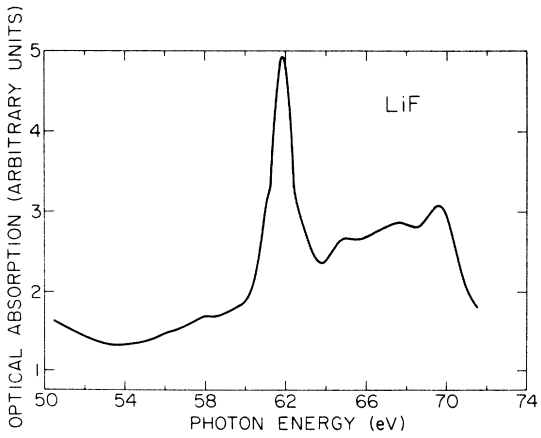

FIG. 1. Absorption coefficient of LiF at the onset of the Li K absorption in arbitrary units.

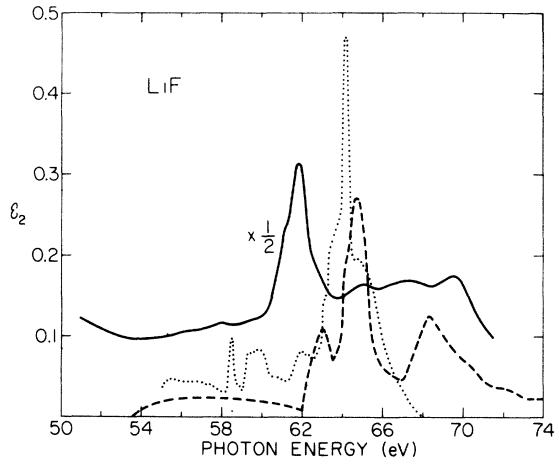

FIG. 2. Experimentally determined ϵ_2 spectrum of LiF near the onset of the Li K absorption in LiF (solid line). Included are the theoretical ϵ_2 spectra given by Menzel *et al.* (Ref. 1) (dotted curve) and Kunz *et al.* (Ref. 2) (dashed curve).

sorption is due to the electronic polaron. The physical process is the excitation of a Li 1s electron and the simultaneous emission of a longitudinal optical exciton.

For an accurate comparison of the absolute values of ϵ_2, the contribution due to valence-band transitions has to be subtracted from the experimental curve. Taking this into account, one finds that the theoretical values for ϵ_2 are about a factor of 2 to 3 larger than the values determined experimentally. In view of the approximations made in the calculations, the agreement between theory and experiment seems to be reasonable, but it is not good enough to support unambiguously the interpretation of the spectrum in terms of a one-electron band model alone.

The author would like to thank F. C. Brown, J. D. Dow, A. B. Kunz, and D. J. Mickish for stimulating discussions. The help of the staff at the University of Wisconsin Physical Sciences Laboratory is greatly appreciated.

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*On leave of absence from the University of Hamburg, Hamburg, Germany.

†Financial support of this research by the U. S. National Science Foundation under Grant No. NSF-GH-33634, the U. S. Army Research Office (Durham) under Contract No. DA-ARO-D31-124-71-G103, and the U. S. Air Force under Contract No. F44620-70-C-0029 is gratefully acknowledged.

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