Li K-edge soft-x-ray absorption in LiF

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The properties of LiF have attracted the attention of theorists for several decades, and previous workers have often regarded the properties of this solid as being somewhat like those of the hydrogen atom: That is, it was assumed that LiF was understood. The purpose of this theoretical study of the soft-x-ray edge of the Li ion in LiF is to demonstrate that this view is unwarranted. This paper concentrates on the effects of exciton structure and multiplicity on the Li K-shell absorption to argue that the simple picture of the LiF soft-x-ray properties may need revision. It is argued that some recent and some old experiments are in accord with the conclusions of this work.

I. INTRODUCTION

The past ten years have produced several band-structure calculations of solid LiF which attempted to describe the optical absorption of this system in terms of the resultant energy bands. These calculations included self-consistent local density calculations by Menzel et al.,[1] and by Zunger and Freeman.[2] There were also two self-consistent Hartree-Fock calculations, one by Mickish et al.,[3] and the other by Euwema et al.[4] In these papers several extremes of interpretation were found. The paper of Euwema et al. was entirely within the framework of the independent particle approximation and provided little information, if any, on optical processes, which they acknowledge. The calculation of Menzel et al. was also entirely within the independent particle framework and tried to explain the optical properties of LiF entirely within the framework of the energy-band picture. This interpretation was shown to be inconsistent with later experimental results involving the comparison of photoemission data with optical absorption properties.[5] The calculations of Zunger and Freeman and of Mickish et al. recognized the need for excitonic corrections as well as other corrections to the energy-band theory and were somewhat more successful in explaining the optical data. The calculation of Mickish et al. and some experiments which supported this model due to Gudat et al.[6] and Sonntag[7] were later questioned in an experimental paper by Fields et al.[8] The calculations of Zunger and Freeman were in general agreement with the experimental data of Fields et al. The basic methods used by Zunger and Freeman ignore any possible multiplet structure in the excitons formed upon exciting the Li K-shell. Furthermore, the experimental analysis due to Fields et al., even though based upon the free Li^+ absorption data reported by C. E. Moore,[9] also completely ignored the possibility of a multiplet structure being involved in the solid-state spectrum. It is the purpose of this paper to demonstrate that ignoring the multiplet structure produces an incomplete analysis, and that if one includes this, then the conclusions reached by Fields et al. may be invalid concerning the LiF Li K-shell absorption in the 58-eV energy range. The present conclusions reached on theoretical grounds alone are consistent with the earlier experimental results of Gudat et al. and of Sonntag. We note that these results are also consistent with recent experiments performed on several samples using several techniques.[10]

This study concerns the formation of core excitons from the Li K-shell. The Li 1s level is a very narrow band state indeed and one may treat its excitons as an impurity in the LiF crystal. In this case we treat the system using the molecular cluster method. The cluster used is a LiF_6^{5-}-cluster embedded in a charge-neutralizing array of point ions which not only provide for charge neutrality of the system as a whole but also provide the proper environmental potential at each ion site. This bounding potential was derived in this form, and its essentialness demonstrated using the local-orbitals framework, by Kunz and Klein.[11] Using this embedded cluster one solves separately for all states in question using the self-consistent unrestricted Hartree-Fock (UHF) method for each state in question. Thus spectral energies are determined by differences in total system energy, not from one-electron eigenvalues as when one uses Koopmans's theorem. We believe that independent particle models, such as the UHF, are needlessly inaccurate for solid-state calculations even when one solves self-consistently for each state in question. Therefore, we enhance our calculations with correlation corrections. These corrections are obtained here by using the UHF virtual orbitals, determined separately for each state, as a basis set with which to perform Rayleigh-Schrödinger perturbation-theory (RSPT) calculations of the correlation energy of each state. Thus the spectral energies are fully correlated. The methods used are briefly described in the following section, along with a numerical test of the free Li^+ ion to establish the accuracy of the method. In Sec. III, the results are presented and compared with current experiment.

II. DISCUSSION OF METHODS EMPLOYED

The basic method is the UHF method. The Hamiltonian for n electrons and N nuclei is given as

$$H = \sum_{i=1}^{n} -\frac{h^2}{2m}\nabla_i^2 - \sum_{i=1}^{n}\sum_{I=1}^{N}\frac{e^2 Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2}\sum_{i,j=1}^{n'}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{I,J=1}^{n'}\frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \quad . \quad (1)$$

In Eq. (1) $\vec{r}_i$ refers to the position of the ith electron. Its mass is m and its charge is e. The position of the Ith nucleus is $\vec{R}_I$ and its atomic number is Z_I. In this work we assume the nuclei are of infinite mass and make the Born-Oppenheimer approximation. If it is necessary to include spin degrees of freedom the coordinate of the ith electron is $\vec{x}_i$. The trial wave function is a single Slater determinant of singly occupied one-electron orbitals. In this limit the n-electron wave function is given as

$$\Psi^\alpha(\vec{x}_1, \ldots, \vec{x}_n) = (n!)^{-1/2}\det|\phi_i^\alpha(\vec{x}_i)| \quad . \quad (2)$$

The one-electron orbitals $\phi_i^\alpha(\vec{x}_i)$ are determined variationally. The defining equation is simply the UHF equation

$$F^\alpha(\rho^\alpha)\phi_i^\alpha(\vec{x}_i) = \epsilon_i^\alpha\phi_i^\alpha(\vec{x}_i) \quad , \quad (3)$$

where

$$F^\alpha = -\frac{h^2}{2m}\nabla_i^2 - \sum_{I=1}^{N}\frac{e^2 Z_I}{|\vec{r}-\vec{R}_I|} + e^2\int\frac{\rho^\alpha(\vec{r}',\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' - e^2\rho^\alpha(\vec{x},\vec{x}')\Big/|\vec{r}-\vec{r}'| + V_{\text{ext}} \quad (4)$$

and

$$\rho^\alpha(\vec{x},\vec{x}') = \sum_{i=1}^{n}\phi_i^\alpha(\vec{x})\phi_i^\alpha\phi_i^{\alpha+}(\vec{x}') \quad . \quad (5)$$

The superscript α is used to indicate that the Fock operator and its first-order density matrix are determined separately for each state in question. The potential V_{ext} is the proper ionic one developed earlier by Kunz and Klein. The one-electron orbitals are expanded in a set of Gaussian-type orbitals. The basic orbitals are the double-zeta sets developed by Huzinaga,[12] and extended here by the addition of diffuse s and p Gaussians to facilitate the description of the F negative ion and also with s, p, and d polarization functions to permit a description of the correlation properties of the system.

In this study results are obtained using second-order RSPT. It has been found by Bartlett and co-workers that this level is able to extract 90% of the correlation contained in a basis set.[13] Such a level of accuracy is quite sufficient for our present needs. We did run some limited tests including third order and found it makes an insignificant difference to the spectroscopic energies. That is, predictions change by far less than 0.1 eV.

The second-order correction to the total energy, E_2^α, is given by the expression

$$E_2^\alpha = \sum_{i>j=1}^{n}\sum_{a>b=n+1}^{\infty}\frac{|V_{ij}^{ab}|^2}{\epsilon_i^\alpha + \epsilon_j^\alpha - \epsilon_a^\alpha - \epsilon_b^\alpha} \quad , \quad (6)$$

where

$$V_{ij}^{ab} = \left\langle\phi_i^\alpha\phi_j^\alpha\left|\frac{e^2}{r_{12}}\right|\phi_a^\alpha\phi_b^\alpha\right\rangle - \left\langle\phi_i^\alpha\phi_j^\alpha\left|\frac{e^2}{r_{12}}\right|\phi_b^\alpha\phi_a^\alpha\right\rangle \quad . \quad (7)$$

A test of this method was initially made for the free Li$^+$ ion. The ground state and the singlet and triplet $1s2s$ excited state were calculated in the UHF and the correlated limit. The results for the transition $1s^2$ to $1s2s$ (^3S) are 58.22, 58.96, and 59.01 eV in the UHF, the correlated, and the experimental[9] limits, respectively. The results for the transition $1s^2$ to $1s2s$ (^1S) are 60.66, 60.70, and 60.75 eV in the UHF, the correlated, and the experimental[9] limits, respectively. These results indicate a significant ability of the present methods to make accurate calculations of the spectral energies. In achieving this accuracy, we use projection operators to prevent excited states of the same symmetry as lower states from collapsing into these lower states, and also we project out the effects of triplet contamination in the excited open-shell singlet. These techniques are undergoing further development and will be the subject of a report when complete.[14] The above test on the Li$^+$ free ion clearly indicates two points. The full model employed is capable of accurately predicting the singlet-triplet splitting (error is 0.02 eV or 1% here), and correlation corrections are essential if one is to obtain accurate multiplet splittings. (The unrestricted Hartree-Fock splitting has an error of 0.68 eV or 35%.)

III. RESULTS FOR LiF AND COMPARISON WITH EXPERIMENT

The methods described in the previous section were employed to obtain the spectrum of the Li$^+$ ion in LiF using the LiF$_6^{5-}$ cluster embedded in a charge array for the ground state and the excited states corresponding to the $^{1,3}S$ and the $^{1,3}P$ states of the free Li ion. Using the Boukaert-Smaluckowski-Wigner (BSW) notation common to the energy-band theory we compute the $^{1,3}\Gamma_1$ and the $^{1,3}\Gamma_{15}$ states in the solid. In the UHF limit these states lie at 57.8, 61.2, 60.6, and 61.4 eV for the $^3\Gamma_1$, $^1\Gamma_1$, $^3\Gamma_{15}$, and $^1\Gamma_{15}$ states, respectively. If correlation is included, these states move to 58.0, 61.6, 61.5, and 62.3 eV, respectively. The computed states lie several eV below the computed ionization limit for the Li$^+$ $1s^2$ state and hence the excited electron and the core hole remain spatially correlated. That is, there is no question as to the excitonic nature of these excitations. Since the ground state of the system is a $^1\Gamma_1$, the only one of these excited states which couples to the ground state by the dipole operator is the $^1\Gamma_{15}$ state. This lies at 62.3 eV and gives a natural explanation for the intense optical absorption peak found near this energy. In

general, most theories and experimental interpretations made recently are in agreement with this point.[8] From here on there is no agreement to be found. The relevant experiments all find a weak absorption feature at about 61 eV, which appears as a shoulder on the 62.3-eV peak in most data.[8,15] The most recent interpretation given this feature is due to Fields *et al.* who believe this to be the transition to the $^1\Gamma_1$ state, that is, the $1s2s$ ^1S excited state of the Li. They base this comparison on the data of C. E. Moore. However, a word of caution is in order here. The $1s2s$ ^1S state of the free Li$^+$ ion is not actually observed in nature but merely inferred since the transition from ^1S to ^1S state is strictly forbidden. It is possible that this state becomes optically accessible in a solid, of course, but an alternate possibility also suggested by the data of C. E. Moore is that one is seeing the transition to the $1s2p$ ^3P state which is found, albeit by indirect means, to lie at 61.27 eV in the case of free Li$^+$.[9] The energy for this transition is computed to be 61.5 eV in the solid and is a possible candidate for the shoulder. Energetics alone cannot rule out the transition to the $1s2s$ ^1S state as the above calculations demonstrate. Likely this shoulder includes components of the $^1\Gamma_1$ and $^3\Gamma_{15}$ state. The mechanisms by which these states could become visible are discussed below.

There remains the $1s2s$ ^3S state to discuss. This state is ignored by all the previous theories. As we have seen, this transition lies at 58.0 eV in the solid according to our calculation. The equivalent transition is predicted by these calculations to lie at 58.96 eV in free space as opposed to 59.01 eV experimentally. There is every expectation that the solid-state value for this excitation may be accurate.

There is one immediately interesting result here. In the solid, the $^1\Gamma_1$-$^3\Gamma_1$ splitting is computed to be 3.6 eV, whereas the $^1\Gamma_{15}$-$^3\Gamma_{15}$ splitting is found to be only 1.0 eV. The equivalent ionic splittings were computed to be only 1.7 eV for the ^1S-^3S splitting (equivalent to the $^1\Gamma$-$^3\Gamma_1$ splitting). We saw that the ionic value was in good agreement with experiment ($\sim 1\%$ error). Why does the solid-state case produce an enhanced exchange splitting? At present an absolute answer is not possible, but the qualitative features of such an answer are to be found in the theory of Aberg and Dehmer for such spectra.[16] They argue (correctly in our opinion) that the F$^-$ ions surrounding the Li$^+$ ions are electrophobic and constrain excited states of Li$^-$ into "inner-well" and "outer-well" states. The excitons are "inner-well" states. The excited orbital in the $^{1,3}\Gamma_1$ state is s like and the six repulsive surrounding F$^-$ ions constrain the excited $2s$ orbital to be more compact than the equivalent $2s$ free ionic orbital. This compaction in turn enhances the exchange-splitting integral [the $G^0(1s,2s)$ term using Slater's notation]. The same enhancement need not occur for the $^{1,3}\Gamma_{15}$ term as the excited orbital is a $2p$-like orbital. The p orbital may orient to point between neighboring fluorines rather than at them and thus need not see the same compaction.

In the present model, UHF + RSPT, it is clear that the lowest excited state with a hole in the Li ion's K-shell is the $1s2s$ (^3S) state which lies at 58.0 eV. This is not a dipole-allowed transition, but it is also not strictly forbidden. This state is observed in the free ion, indirectly, and

may be accessible in solid-state absorption experiments. We believe that the broadened features seen in optical absorption centering about 58 eV by Gudat *et al.*[6] and by Sonntag[7] may be evidence for this state in the solid case. Recent measurements by the groups of Chiang and Brown reported elsewhere in this issue[10] also find a weak absorption feature at about 58 eV. This is further evidence of the existence of the ^3S state in the spectrum of the LiF crystal.

It is futile to speculate as to why the weak absorption at 58 eV was not observed by the previous measurements of Fields *et al.*,[8] F. C. Brown *et al.*,[15] or Haensel *et al.*[15] One must acknowledge that such weak absorption edges are difficult to observe if sample homogeneity is poor or if insufficient resolution is obtained for any reason in the experimental setup. There remains to be discussed the question of the intensity of the several states as they are accessed by optical means from the ground state.

We computed that low-lying excited states of Li$^+$ in LiF lie at 58.0, 61.6, 61.5, and 62.3 eV for the $^3\Gamma_1$, $^1\Gamma_1$, $^3\Gamma_{15}$, and $^1\Gamma_{15}$ levels, respectively. Of these levels only the $^1\Gamma_{15}$ level lying at 62.3 eV can be reached from the $^1\Gamma_1$ ground state by an optical dipole transition. This level undoubtedly accounts for the strong transition seen experimentally at about 62 eV. There is a rather weak shoulder on the 62-eV peak at about 61 eV. On energetic grounds alone, this could be due to either the $^1\Gamma_1$ or the $^3\Gamma_{15}$ level. The analysis provided by Fields *et al.* assigns this structure to the $^1\Gamma_1$ level. The equivalent free-ionic state has not been seen as the transition in question is $^1S_0\rightarrow{}^1S_0$, a strictly forbidden transition. The free-ion transition $^1S_0\rightarrow{}^3P_{0,1,2}$ has also not been observed although magnetic interactions make it weakly allowed. We shall examine the mechanisms by which the transition into the $^1\Gamma_1$ or $^3\Gamma_{15}$ level become allowed in the solid and estimate the oscillator strength ratio compared to the transition into the $^1\Gamma_{15}$ level.

The analysis used here, which we explain now, was suggested to the authors by D. R. Beck.[17] The $^3\Gamma_{15}$ level can become accessible from the $^1\Gamma_1$ level by a dipole transition if the $^3\Gamma_{15}$ level acquires some $^1\Gamma_{15}$ contamination. This is provided, if at all, by means of a spin-orbit interaction involving the $2p$ level of the Li$^+$. At present a full-scale solid-state estimate is not practical, but one can make one for the free ion. The spin-orbit question in Li$^+$ has been examined originally by Breit;[18] we follow a simplified version given by Condon and Shortley[19] and by Bethe and Salpeter.[20] One may compute the spin-orbit parameter α_{2p} for the $2p$ level of Li$^+$ using the hydrogenic formulas (4^59 and $1^{11}6$ of Condon and Shortley), which yields 2.5×10^{-3} eV for Li$^+$. That this is an underestimate is likely for two reasons: The first is that due to the electrophobic nature of the F$^-$ cage surrounding the Li$^+$ ion the Li$^+$ orbital is not quite as extended as in free space and is thus a bit larger near the nucleus where spin-orbit interactions arise.[16] The second is that the orthogonalization of the Li $2p$ orbital to all neighboring occupied levels also enhances the spin-orbit splitting,[21] a well-known phenomenon in alkali-halide spectroscopy. One may use this parameter in intermediate coupling theory and the intermediate coupling matrices for the configura-

TABLE I. The evolution of the $1s2s$ ($^{1,3}\Gamma_1$) and the $1s2p$ ($^{1,3}\Gamma_{15}$) manifolds of the Li^+ ion in LiF are shown as one adds spin-orbit and "Stark" interactions. The schematic wave functions ψ have the dominant term with unit weight and the weaker members preceded by a generic small coefficient, ϵ_M for spin orbit, ϵ_S for "Stark" effects. Each ϵ in practice is distinct. Details of this are given in the text. ψ_m is the wave function including spin-orbit effect, ψ_S includes "Stark" effect, and ψ_T includes both. In obtaining the schematic, one applies the larger ("Stark" perturbation) first.

Parent state	ψ_m	ψ_S	ψ_T
$^3\Gamma_1$	$^3\Gamma_1$	$^3\Gamma_1 + \epsilon_S\,^3\Gamma_{15}$	$^3\Gamma_1 + \epsilon_S\,^3\Gamma_{15} + \epsilon_m\epsilon_S\,^1\Gamma_{15}$
$^1\Gamma_1$	$^1\Gamma_1$	$^1\Gamma_1 + \epsilon_S\,^1\Gamma_{15}$	$^1\Gamma_1 + \epsilon_S\,^1\Gamma_{15} + \epsilon_m\epsilon_S\,^3\Gamma_{15}$
$^3\Gamma_{15}$	$^3\Gamma_{15} + \epsilon_m\,^1\Gamma_{15}$	$^3\Gamma_{15} + \epsilon_S\,^3\Gamma_1$	$^3\Gamma_{15} + \epsilon_m\,^1\Gamma_{15} + \epsilon_S\,^3\Gamma_1$
$^1\Gamma_{15}$	$^1\Gamma_{15} + \epsilon_m\,^3\Gamma_{15}$	$^1\Gamma_{15} + \epsilon_S\,^1\Gamma_1$	$^1\Gamma_{15} + \epsilon_m\,^3\Gamma_{15} + \epsilon_S\,^1\Gamma_1$

tion SP (Table I) of Condon and Shortley to estimate the fractional character of $^1\Gamma_{15}$ level in the $^3\Gamma_{15}$ level in the $^3\Gamma_{15}$ state. If one does so the $^3\Gamma_{15}$ level is found to have 0.2% $^1\Gamma_{15}$ character, when one uses the electrostatic splitting for the $^1\Gamma_{15}$ and $^3\Gamma_{15}$ multiplets computed here. Magnetic interaction alone does not mix $^1\Gamma_{15}$ character into the $^1\Gamma_1$ or the $^3\Gamma_1$ levels. This is seen schematically in Table I.

At this point after use of magnetic interaction, we find only $^1\Gamma_{15}$ and $^3\Gamma_{15}$ accessible from the ground state by means of dipolar transitions. If one is to observe transitions into the $^3\Gamma_1$ or $^1\Gamma_1$ states, one needs a perturbation which causes mixing of states of different parity. An effect which provides such a mixing is the Stark effect. In LiF, the Li^+ ion at its equilibrium position sits in a centrosymmetric site and the eigenstates are eigenstates of parity. This is no longer true if the Li^+ ion moves from its average position. Thus any motion of Li^+ from a centrosymmetric site is equivalent in some way to a Stark effect. Such motions occur naturally in LiF due to the zero-point vibrational motion of the rather light-mass Li^+ ions. One may use simple models of the ion-ion interaction in LiF to estimate that the Li^+ ion moves of the order of 10% of the Li-F distance in its zero point motion.[22] We are able to estimate the magnitude of this effect by moving the Li^+ ion around in its unit cell using our cluster calculation. We find for motion in the (100) direction there is 15% p admixture in the $2s$ orbitals for a displacement of 10% of the Li-F distance, an 8% admixture for a 5% displacement, and a 4% admixture for a 2.5% displacement. In both the (110) and (111) directions there is a 15% admixture for a 10% displacement as well. Thus if we use the old concept of a configuration coordinate diagram and the Frank-Condon principle,[23] there is a significant p admixture in the S levels for Li^+ in LiF or likely in similar solids. A rough average here says there is about 10% p character on the average in the s levels. Thus we find the transition to the $^1\Gamma_1$ level is made allowed by an admixture of $^1\Gamma_{15}$ states due to zero-point motion of the Li^+ ion. Furthermore, transitions into the $^3\Gamma_1$ level become allowed by means of a double perturbation. Spin-orbit effects mix the $^1\Gamma_{15}$ level into the $^3\Gamma_1$ level. Therefore, a situation exists in which one may access the $^1\Gamma_{15}$, $^3\Gamma_{15}$, $^1\Gamma_1$, and $^3\Gamma_1$, the relative $^1\Gamma_{15}$ weights being about 1.0, 2×10^{-3}, 10^{-1}, and 2×10^{-4}, respectively, based upon these crude estimates. These results, along with energetic considerations, suggest that the large peak

at 62 eV is due to the $^1\Gamma_{15}$ level, the shoulder at 61 eV is largely but not exclusively due to the $^1\Gamma_1$ state with some $^3\Gamma_{15}$ character, and the very weak elusive feature at 58 eV may well be due to the $^3\Gamma_1$ level. The "Stark" perturbation effect is shown schematically in Table I.

To conclude this section, we observe that for reasons given earlier, the spin-orbit effect may well be larger than estimated. There is also another solid-state effect not yet discussed that could lead to this conclusion. In addition to configuration mixing between the $^1\Gamma_{15}$ and $^3\Gamma_{15}$ states of Li^+, one also has in the solid the continuum of $^1\Gamma_{15}$ like excited states from the F^- $2p$ or $2s$ shells, some of which are nearly degenerate with the $^3\Gamma_{15}$ level and could produce some additional $^1\Gamma_{15}$ character in the ionic $^3\Gamma_{15}$ level. This size of such an effect is unknown, but there is no reason to believe it to be negligible. This is certainly a possibility for future study.

IV. CONCLUSIONS

We conclude that multiplet splittings are of sufficient size to be observable in the Li^+ K-shell optical absorption in the LiF crystal. Furthermore, we believe that there is sufficient evidence from both recent and past experiments to indicate that such structure may have been observed. We further conclude that the observed absorption is into excitonic states which are well bound with respect to the pertinent band edge. The bindings for the states considered range from 1.0—5.5 eV. We believe the binding energies and the multiplet structure may be understood in terms of a relatively straightforward calculation. Until the exact transition matrix elements are computed, the ability to see the Li^+ multiplets in LiF optically, as opposed to their simply being eigenstates of the system not involved in the optical process remains tentative. Nonetheless, simple energetics and qualitative oscillator strength arguments lead us to believe that the 58-eV feature is due to the $^3\Gamma_1$ level and the 61-eV feature may be due in some part to the $^3\Gamma_{15}$ level as well as the $^1\Gamma_1$ level as discussed by other authors.

We conclude that the use of a symmetry-projected UHF model augmented by application of low-order RSPT calculations using the UHF virtual orbitals, developed separately for each state in question, is a reasonably straightforward way to implement a cluster study of these properties. The amount of computer time is not trivial. In the present case we spent several days of computer time

using a VAX 11-750. Nonetheless, the results fully justify the expense in our opinion. Recently we have been able to perform similar calculations on an FPS-164 attached processor. The reduction in computer time required to several hours is further evidence of the future practicality of such nonparametrized methods.

ACKNOWLEDGMENTS

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