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Semiempirical Molecular-Orbital Treatment of the *U* Band in LiF : H$^-$

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(Received 26 July 1971)

Calculations using the semiempirical self-consistent-field procedure known as complete neglect of differential overlap (CNDO) have been made on a collection of lithium and fluorine atoms in an attempt to generate a model of the *U* center. The system consists of 27 atoms arranged in a fcc lattice. The central fluorine atom is replaced by a hydrogen atom, simulating the *U* center. Calculation of the CNDO eigenvalue spectrum for this "molecular" model shows that the essential features of this defect are represented very well and that the value obtained for the *U*-band excitation energy compares well with empirical and other theoretical data.

I. INTRODUCTION

In a previous study[1] I investigated the feasibility of utilizing a very simple "molecular" semiempirical self-consistent-field (SCF) procedure for the calculation of the electronic structure of ionic crystals. Pilot calculations on LiF using the complete neglect of differential overlap (CNDO) method gave very encouraging results for the bandwidths and band gaps generated from model systems containing up to 18 atoms. Later calculations[2] have extended the size of the model system to 27 atoms, with a consequent increase in the accuracy of the description of the band structure.

The applicability of the CNDO procedure to the calculation of the electronic structure of solids has been supported by the recent work of André *et al.*[3] in their comparative study of extended Hückel, CNDO, and *ab initio* calculations of the band structures of polyene and polyethylene. As these authors point out, the results of semiempirical calculations must be treated with some reserve, however, the relative band characteristics are described reasonably well by the CNDO method when compared to *ab initio* calculations. This is particularly true in the region around the Fermi level, which is where our interest lies in the current calculations. Since *ab initio* calculations on the systems being investigated here are not feasible at the present time, and in the light of previous experience, we feel that the use of the CNDO approximation in this case is justifiable.

In this work we have studied one of the simplest defects in the alkali halides—that of the *U* center.

There are three well-known *U* centers: the original *U* center, consisting of a hydride ion substituted at a halogen ion site; the U_1 center formed by the inclusion of a hydride ion at an interstitial point in the host lattice; and the U_2 center in which a hydrogen *atom* is substituted for a halogen ion at the halogen site. Here, we shall only be concerned with the first of these three, and reference to a *U* center will denote a substitutional hydride ion.

There has been continued interest in these defects, both theoretically and experimentally, in recent years. The experimental investigations have been centered around the "local modes" of the system, which is a vibronic effect[4] giving rise to a characteristic infrared spectrum, while the classical studies of Hilsch and Pohl[5] and Delbecq *et al.*[6] provide information on the absorption spectrum for the *U* bands in some alkali halides.

Most previous theoretical investigations of *U* centers have used the point-ion model of Gourary[7] in which the H^- is coupled to the lattice with a Madelung-type potential (crystal-field approximation). This approach has given considerable insight into the structure of the *U* center but, unfortunately, the results for *U*-band excitation energies are of the order of 15% lower as compared to experimental data. For crystals not having experimental data, the results may be compared to those obtained by Ivey's law,[8] derived from empirical data, with approximately the same result. A more recent calculation of the electronic structure of the *U* center has been made by Spector *et al.*,[9] again using the point-ion model, which confirms Gourary's results over the whole range of alkali halides, including those crystals having CsCl structure. This study also includes investigations involving excited states of the hydride ion. Approaches using the continuum model have not proved very effective in treating this type of defect. Simpson's calculations on the U_2 center in KCl[10] have shown that the model does not take into account variation of the dielectric constant away from the trapping center.

The use of the "molecular model" approach to study defects in crystals is not new; considerable work was done[11] in Japan concerning linear-combination-of-atomic-orbitals (LCAO) calculations on *F* centers. These calculations were performed closely following Löwdin's[12] LCAO work on "pure" alkali halides. In a future communication we hope to report calculations on *F*, *F′*, and F_A centers, the results of which may then be compared with these earlier calculations.

The present work is confined to studies of the ground state of LiF:H^- (here we use the conventional form of indicating an H^- substitution in an LiF host lattice). In principal, the technique is applicable to systems involving heavier ions, but computational limitations preclude this at the present time.

II. METHOD OF CALCULATION

The details of the CNDO method have been documented elsewhere.[13] In the calculations reported here we have used the CNDO/2 parametrization and it should be noted that the CNDO parameters for second-row atoms have been revised by Weiss *et al.*[14] in order to avoid a difficulty concerning rotational invariance.

We have used a modified version of a program written originally by Dobosh which is available through the Quantum Chemistry Program Exchange scheme.[15] The original program was capable of handling systems having up to 35 atoms with a total of 80 orbitals. For the present calculations involving cubic structures of 27 atoms, we have extended the program to allow up to 120 basis functions. In this form the program was run in extra large core on the IBM 360/65 of the University of Florida Computing Center.

In order to simulate the crystal using the "molecular" approximation we have used the system shown in Fig. 1. This is a cube having 27 atoms, 14 lithium and 13 flourine. The coordinate system has been located upon the central flourine atom. This then maintains the symmetry of the defect center as T_d, that of the host lattice. In all of the calculations reported here, we have constrained the interionic separation at the equilibrium value for the "pure" crystal 2.01 Å.[16] The *U* center is simulated by replacing the central flourine atom by a hydrogen atom. The total charge of the system is maintained at + 1 in order to give a closed-shell ground-state configuration.

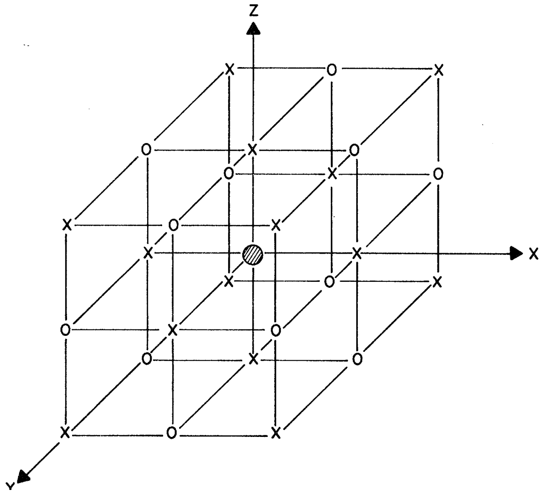

FIG. 1. Coordinate system used for calculations on LiF and LiF:H^-. The central atom, denoted by a closed circle, is flourine in LiF and hydrogen in LiF:H^-; lithium atoms are denoted by crosses; and flourine atoms are denoted by open circles.

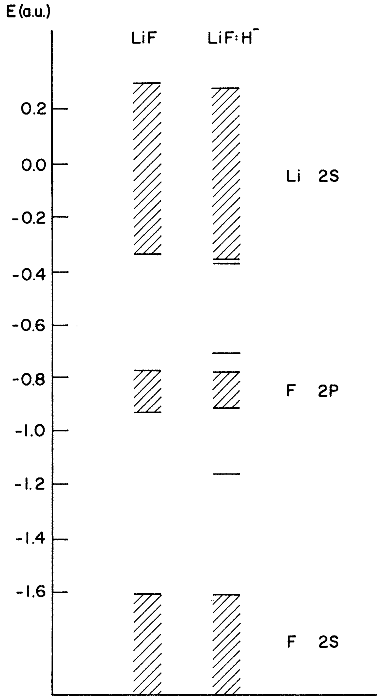

FIG. 2. Eigenvalue spectra for LiF and LiF:H$^-$ at an internuclear separation of 2.01 Å.

III. RESULTS AND DISCUSSION

The eigenvalue spectra calculated for the *U* center is shown in Fig. 2, along with that of the "pure" crystal, for comparison. The individual eigenvalues within the bands have not been shown in this figure due to the high density concomitant with calculations involving 108 and 105 basis functions for LiF and LiF:H$^-$, respectively.

The eigenvalue spectrum shown for LiF gives a valence bandwidth of 4.03 eV and a valence band–conduction band gap of 12.15 eV. These data may be compared with the experimental result of 13.6 eV for the band gap[17] and with previous theoretical results of 15.0 eV from the tight-binding calculation of Lafon *et al.*[18] and 12.8 eV from the mixed basis calculation of Kunz *et al.*[17] The valence bandwidth may be compared to the results of Ewing and Seitz[19] of 3.9 eV and Kunz *et al.*[17] of 2.3 eV. It should be noted that the interpretation of the experimental results for the band gap is rather complicated due to the unusually strong exciton structure at the low-energy edge of the absorption edge. A full discussion of this point is given by Kunz *et al.*[17]

The over-all integrity of the eigenvalue spectrum is maintained for LiF:H$^-$. The valence band shows a slight decrease in width to 3.53 eV, while the conduction band remains virtually unaltered, with a shift to lower energy of some 0.78 eV. The effects of the introduction of the hydrogen are to be seen in the three levels which lie in the interband regions. The lower level arises from a hydrogen 1*s* and is occupied, having taken the place of the removed flourine 2*s* level. The two levels lying in the valence conduction band gap are the ones of interest. The lower of these levels arises from a loosely bound hydrogen 1*s* state, giving rise to the H$^-$ ion in the crystal. The higher level arises from the unoccupied Li 2*s* levels which may be associated, via inspection of the relevant eigenvectors, with the six nearest-neighbor lithium atoms. It is somewhat arbitrary to separate this level from the 2*s* conduction band which is due to the remaining unoccupied lithium 2*s* levels. We have done so since this accentuates the simple model of the trapped electron on H$^-$ as being associated with only the nearest-neighbor anions. Excitations from the H 1*s* level to this level have an energy of 9.15 eV or 135.5 mμ. This excitation energy then gives the characteristic *U* band in the uv spectrum of LiF:H$^-$. The values of this excitation energy for LiF:H$^-$ have not been determined experimentally. However, Ivey's empirical law[8] $[\lambda(\mathrm{m}\mu)=6.5a^{(1.1)}$, where a is the internuclear separation in Å] gives an excitation energy of 9.45 eV while the point-ion calculations of Spector *et al.* give 8.11 eV. No other data seem to be available on the position of the *U* band in LiF:H$^-$, but the results of this calculation certainly lie well within previously obtained values and are closer to the empirical value than those of the point-ion calculations.

Part of the success of this approach in describing the *U* center probably lies in the localized nature of this defect. This enables the molecular system to encompass the defect sufficiently to allow reasonable results. We are now testing this approach on some *F* centers in LiF in order to test further the applicability of the CNDO approach to such problems.

IV. CONCLUSIONS

The CNDO calculations of the *U* band in LiF:H$^-$ have proved rather successful. This, coupled with earlier work on the band structure of LiF, has shown that the "molecular" CNDO approach may be useful in applications to crystalline solids. In particular, we would expect reasonable results for systems showing highly localized properties. We are now investigating the *F*-center-type defects in LiF in order to ascertain the success of this method in these cases.

ACKNOWLEDGMENTS

Thanks are extended to Professor P. O. Löwdin and members of the Quantum Theory Project, University of Florida, for their kindness and hospitality. Thanks are also due to Dr. J. R. Sabin for the use of the CNDO/2 program.

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PHYSICAL REVIEW B VOLUME 5, NUMBER 2 15 JANUARY 1972

Frequency Distribution of Phonons in a Ballistic Heat Pulse Determined by Magnetic Resonance

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(Received 24 May 1971)

The scattering of ballistic heat pulses by resonant spins in MgO : Fe^{2+}, tuneable with a magnetic field, has been used to investigate the phonon frequency spectrum of the heat pulses at helium temperatures. A magnetic field of 60 kOe allowed phonons with frequencies up to 288 GHz to be studied. Good agreement was obtained with a Little-type calculation based on an acoustic-impedance model of interfacial thermal conduction. It is suggested that the lack of such agreement by most previous workers has often been due to inadequate preparation of surfaces.

I. INTRODUCTION

The method of heat pulses is now well established as a valuable technique for studying phonons in the frequency range 10–1000 GHz.[1] Its use has been considerably restricted, however, by uncertainty regarding the exact frequency spectrum of the phonons emitted into the specimen by the heat-pulse generator. Usually it has been assumed, following the theory of Little,[2] that

$$\rho(\nu)d\nu=\frac{2\pi k^4 A}{h^3}\left(\frac{\Gamma_l}{V_l^2}+\frac{\Gamma_{t1}+\Gamma_{t2}}{V_t^2}\right)\times\left(\frac{1}{e^{h\nu/k\theta}-1}-\frac{1}{e^{h\nu/kT}-1}\right)\nu^2 d\nu\;, \qquad (1)$$

where $\rho(\nu)$ is the distribution of heat-pulse phonons as a function of frequency ν. In this expression, θ is the excitation temperature of the heat-pulse generator, T the ambient temperature of the specimen, A the contact area between generator and specimen, V_l and V_t the longitudinal and transverse acoustic velocities, and Γ_l, Γ_{t1}, and Γ_{t2} the phonon transmission coefficients for, respectively, longitudinal modes, transverse modes polarized in the plane of the interface, and transverse modes polarized normal to this plane. By the integration of (1) over all phonon frequencies an expression can be obtained which relates θ with P, the power dissipated in the heat-pulse generator

$$P=\left(\frac{2\pi^5}{15}\right)\frac{k^4}{h^3}A\left(\frac{\Gamma_l}{V_l^2}+\frac{\Gamma_{t1}+\Gamma_{t2}}{V_t^2}\right)(\theta^4-T^4)\;. \qquad (2)$$

This method of determining θ is unsatisfactory, however, because of the present lack of reliable values for Γ_l, Γ_{t1}, Γ_{t2} for any materials. A few thermal-conductivity measurements have been made of interfacial thermal conductance κ which is defined by $P=\kappa A\;(\theta-T)$ for $(\theta-T)\ll 1$, and therefore gives the proportionality constant in (2). Unfortunately, the experimental technique is a difficult one since it involves the extrapolation of temperature grad-