Another factor which tends to reduce the observed shoulders may be mentioned. Experimentally, the backscattered particles within a certain energy window are counted, and thus the measured yield will be inversely proportional to the stopping power. In the shoulder region the increase above normal scattering yield may thus partly be compensated by a higher-than-normal energy-loss rate.

In view of these uncertainties in the measured curves, a further refinement of the calculations may not be too promising. It might, however, be relatively straightforward to include the effect of thermal vibrations on the planar average potential, as suggested by Erginsoy.[4] A simple estimate of the minimum yield $\chi_{\min}$ based on formula (7) suggests that $\chi_{\min}$ is inversely proportional to the square root of the slope of the potential at distances $\lesssim\rho$ from the plane. According to Fig. 27 of Ref. 4, the introduction of a temperature-dependent potential may then lead to a relative increase in the calculated minimum yield of the order of 50%. This could lead to a significant improvement in the agreement with experimental results.

V. CONCLUSIONS

Despite significant discrepancies between the calculated and measured angular distributions, the calculations are still quite successful in predicting the angular width. The functional dependence on atomic number Z_1 and Z_2 of projectile and lattice atoms, projectile energy E, and planar spacing d_p is in good agreement with measurements, and formula (9) for ψ_p gives a useful estimate of the absolute magnitude of the critical angle. The measured critical angles were in general smaller by 20–25% in the investigated semiconductor crystals.

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Calculation of Electronic States of Li_2^+ as a Free Ion and in a Point-Ion Lattice*

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Electronic structures for the Li_2^+ molecule ion have been calculated using Hartree-Fock-Roothaan methods. Ground-state and several excited-state energies have been obtained for various internuclear distances for the Li_2^+ as both a free ion and as a substitutional defect in a point-ion crystal lattice. The present calculation gives a ground-state binding energy for the free ion of 1.24 eV, which is in agreement with a calculation by James. In a crystal-lattice environment, equilibrium internuclear distances are about 4.0 a.u. for the ground and the first few excited states, with a transition energy of no more than 0.9 eV for the first allowed transition. These results do not support the suggestion by Farge that the optical-absorption peak at 2.25 eV and the associated fluorescence at 1.36 eV, observed in irradiated LiF, are due to the Li_2^+ defect.

INTRODUCTION

One of the defects which occurs in alkali-halide lattices consists of a pair of alkali-metal atoms occupying a single cation site. Molecule ions of this sort which have a small number of electrons, for example, Li_2^+ in a LiF lattice, are susceptible to electronic structure calculations using molecular-orbital methods. Calculated energy separations between states may be compared with experimental values obtained from optical absorption and luminescence spectra.

Calculations have been carried out, using linear combination of atomic orbitals–molecular orbital–self-consistant field (LCAO-MO-SCF) methods for the $^2\Sigma_g^+$ ground state and the first few excited states of Li_2^+, both as a free ion and as a substitutional defect in a point-ion lattice. Free-ion calculations have previously been performed by James[1] and by Pfeiffer and Ellison[2]

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and the agreement between their results and ours is good. The results of the calculations for the defect in the lattice are presented in the form of curves of energy as a function of distance between the defect nuclei. The results of this calculation are compared with the small amount of available experimental data.

To perform SCF-MO calculations the CDC 6600 version of the open shell part of the POLYATOM system of computer programs[3] was used in which the open-shell procedure suggested by Roothaan[4] is followed. A general description of the programs may be found in Csizmadia *et al.*[5] These programs employ Gaussian basis functions. Even with large numbers of functions, the Gaussian basis provides a poor representation of 1σ core states. However, this problem is not expected to affect significantly the relative energies which we wish to calculate. The *s*-type and *p*-type basis functions used were taken from work of Huzinaga[6] and Csizmadia,[7] respectively, and are listed in Table I.

TABLE I. Gaussian orbital exponents.

Type	Orbital exponents
s	0.0286
	0.0767
	0.4446
	1.1568
	3.1579
	9.3533
	31.9415
	138.7295
	921.2708
p	0.0160
	0.0550
	0.1880
	0.6520
	2.2600

First the total energy was calculated as a function of internuclear separation for the ${}^2\Sigma_g^+$ ground state and the ${}^2\Sigma_u^+$ first excited state of the free Li_2^+ ion. A basis set of 28 functions was used, nine *s*-type and five *p*-type on each Li nucleus. *p*-type functions were included to allow for distortion of the charge along the molecular axis.

To include the Coulomb effects of the lattice on the Li_2^+ electronic wave function, the ion was placed in a $\langle 110 \rangle$ orientation in a number of lattices, each of about 700 point ions. SCF calculations were then carried out for varying separation of the defect nuclei. No additional basis functions were placed on any of these 700 ions, but the basis was increased to 48 functions to include Π states in the lower symmetry of the lattice. The ground state ${}^2\Sigma_g^+$, and ${}^2\Sigma_g^+$, ${}^2\Sigma_u^+$, ${}^2\Pi_u$, and ${}^2\Pi_g$ lowest-lying excited states were calculated for each lattice.

The first calculation was made with a lattice that was neutral when the defect was included and was symmetrical about a body-centered interstitial position. Using the first 32 shells about this position, one obtains a lattice of 720 point ions. The second lattice used was obtained by removing the three outermost shells, resulting in a lattice of 672 points ions. This was done to determine the sensitivity of the electronic structure to the size of the lattice. Both of these lattices were asymmetrical about the defect. To obtain a symmetrical lattice, 32 shells about a Li^+ site (the center of the molecule-ion defect) were taken to generate 738 ions with a net charge of -1 including the defect. Calculations employing these various lattices were compared to determine whether boundary or asymmetry effects were large enough to affect the spacing of the electronic energy levels in any important way.

Because positive Li ions are near neighbors along the defect axis for the $\langle 110 \rangle$ orientation, large relaxations of lattice ions are to be expected. More than 100 ions of the 738 ion lattices were placed in relaxed positions for a further set of SCF calculations. The relaxation parameters were supplied by Dellin *et al.*,[8] from a calculation using the method of Hatcher and Dienes.[9] In this type of calculation, Coulomb forces and two-body repulsive interactions are taken into account using a point-ion model with dipole polarizabilities assigned to both defect and host-lattice point ions. The wave function which we obtained for the Li_2^+ in the environment of the unrelaxed lattice was used to determine the polarizability of the Li_2^+, which was required for the Hatcher-Dienes calculation. The repulsive interactions not available from perfect crystal data were estimated by Dellin *et al.*[8] using methods similar to those used in the *H*-center calculation of Dienes *et al.*[10]

The spatial dependence and magnitude of the electric field near the defect are probably adequately described by the relaxed point-ion environment. However, the magnitude of the potential at the defect site is affected by the slow convergence of the lattice sums. This magnitude can be corrected by determining the potential at the defect site due to the point ions and increasing or decreasing it by the amount of its difference from the Madelung potential. This correction may be applied to the one-electron energies.

RESULTS

In Fig. 1 we have plotted the energy of the Li_2^+ free ion versus internuclear separation for the ${}^2\Sigma_g^+$ ground state and the ${}^2\Sigma_u^+$ first excited state. The value for the binding energy found by James[1] is indicated and the

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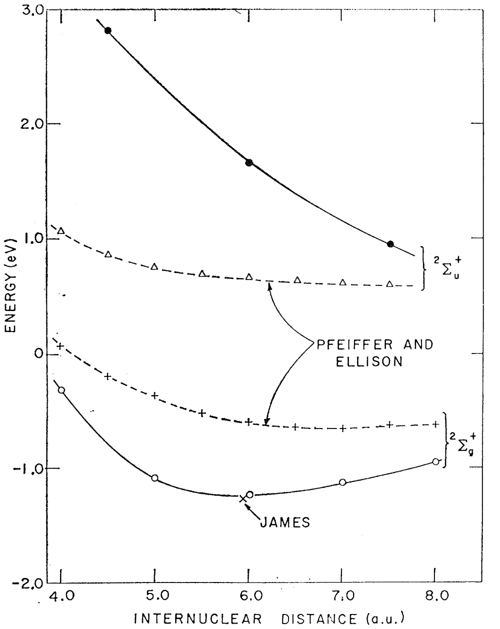

FIG. 1. Li_2^+ binding energy versus internuclear-distance curves for the free ion. The lower $^2\Sigma_g^+$ curve and the upper $^2\Sigma_u^+$ curve represent the results of the present calculation. The other two curves are from Ref. 4. James's result (Ref. 3) is shown as a cross near the minimum of the lower curve.

curves of Pfeiffer and Ellison[2] are also shown. All energies are relative to the sum of the separated energies of Li +Li^+ (calculated to be −7.43222 and −7.23599 a.u., respectively). For the binding energy we obtain 1.24 eV at $R=5.7$ a.u. while James[1] obtained 1.234 eV at 5.96 a.u. and Pfeiffer and Ellison[2] obtained 0.646 eV at 7.0 a.u. The $^2\Sigma_w^+$ lowest-lying excited state $(1\sigma_g)^2(1\sigma_w)^2 2\sigma_w$ is repulsive.

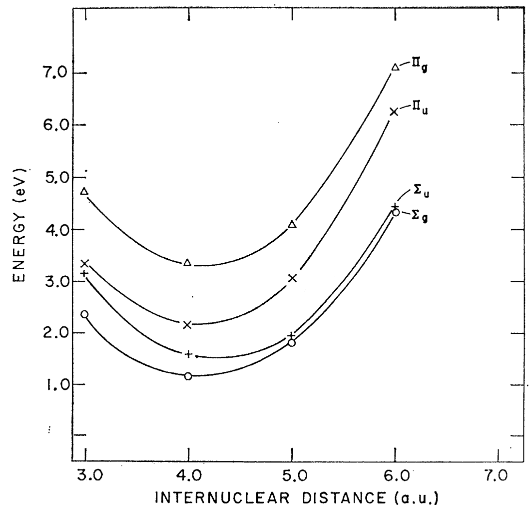

FIG. 2. Plots of total energy versus internuclear distance for Li_2^+ in the unrelaxed 720-ion lattice for the electronic states $^2\Sigma_g^+$, $^2\Sigma_u^+$, $^2\Pi_u^+$, and $^2\Pi_g^+$.

TABLE II. Electronic transition energies (in eV) for Li_2^+ in different lattices near $R=4.0$ a.u.

Transition Ground state	Excited state	720-ion unrelaxed lattice	738-ion unrelaxed lattice	738-ion relaxed lattice
$^2\Sigma_g^+ \rightarrow$	$^2\Sigma_u^+$	0.46	0.37	0.90
$^2\Sigma_g^+ \rightarrow$	$^2\Pi_u$	1.01	1.06	1.25
$^2\Sigma_g^+ \rightarrow$	$^2\Pi_g$	2.22	2.08	2.31
$^2\Sigma_g^+ \rightarrow$	$^2\Sigma_g^+$	···	(1.39)	(1.33)

In Fig. 2 the total energy of the Li_2^+ ion plus that of the 720 point-ion lattice is plotted at various internuclear separations of the defect. This is done for the unrelaxed lattice for several electronic states of the system. For all cases, the zero of energy is arbitrary since only energy differences between the states are of interest here. The three unrelaxed lattices yielded almost identical curves, and for this reason only the 720-ion case is plotted. In determining energy curves, effects of changes in correlation energy have been ignored.

A comparison of Fig. 2 with Fig. 1 brings out the effect of the lattice environment on Li_2^+. The ion has contracted and the new ground-state minimum is at 4.0 a.u. compared to 5.7 a.u. for the free ion. Furthermore, there are now stable excited states in the lattice. The minima for the excited states occur at about the same internuclear separation as the ground state.

For an internuclear separation of 4.0 a.u., near the energy minima, the energies of both allowed and forbidden electronic transitions are given in Table II. Values are given for two of the unrelaxed cases and for the relaxed case (for which $R=3.9$ a.u.). The transition to the lowest $^2\Sigma_g^+$ excited state is included in parentheses since our calculations indicate that the valence electron is unbound (for the unrelaxed lattice case) and may not be bound for the relaxed case (our calculation actually does show a binding energy of 0.05 eV). Thus, with the inclusion of this $^2\Sigma_g^+$ excited state, all transitions to low-lying bound excited states of Σ type in both relaxed and unrelaxed environments are included.

Table III gives the orbital energies of the valence electron for the various states. These energies were obtained by adjusting the SCF values by corrections which are the differences between the calculated potentials and the Madelung potential $-\alpha/a$ at the Li^+

TABLE III. Orbital energies (in eV) of the valence electron near $R=4.0$ a.u.

Configuration	720-ion unrelaxed lattice	738-ion unrelaxed lattice	738-ion relaxed lattice
$^2\Sigma_g^+$ (ground state)	−3.78	−3.79	−3.92
$^2\Sigma_u^+$	−3.35	−3.43	−3.05
$^2\Pi_u$	−2.77	−2.72	−2.68
$^2\Pi_g$	−1.55	−1.71	−0.16
$^2\Sigma_g^+$	···	+0.15	−0.05

ion site. Here α is the Madelung constant for the NaCl structure and a is the interionic distance.

SUMMARY AND DISCUSSION

Results have been presented for Li_2^+ both as a free ion and as a defect in a point-ion lattice environment. As an indication of the accuracy of the energies obtained, results may be compared with those of James[1] and of Pfeiffer and Ellison.[2] At a separation of about 6 a.u., the open-shell SCF procedure yielded a binding energy of 1.225 eV which is close to the value 1.243 eV which James obtained employing the James-Coolidge[11] method. Pfeiffer and Ellison[2] obtained a minimum near 7.0 a.u. with a binding energy of 0.646 eV using the method of diatomics in molecules, which is of more limited accuracy than either of the other methods.

The calculations which include the lattice are an attempt to determine the electronic energies of various sites of the defect in the crystal. Preliminary calculations suggest that a lattice of about 700 ions gives rise to a potential which is in good agreement with the Ewald potential near the center of the lattice, aside from boundary effects which have been taken into account separately. Since calculations were also performed with the point ions in relaxed positions, which does change the crystal field substantially from the unrelaxed case, a good indication of the effect of changes in the crystal field on the electronic transition energies is obtained. Effects of finite size of near-neighbor ions on the electronic configuration of the Li_2^+ ion have been neglected.

For the free-ion case, even the lowest-lying excited state ($^2\Sigma_u^+$) is repulsive, which agrees with the results of Pfeiffer and Ellison.[2] In the lattice, minimum energy in the ground state occurs for a separation of only 4.0 a.u. About the same value for the separation is obtained for each of the first few excited states.

Farge *et al.*[12] have suggested the formation of a Li_2^+ molecule ion at an Li^+ site in LiF crystals irradiated with thermal neutrons or electrons of 1.4-MeV energy. This defect, the antimorph of the *H* center, was suggested to account for a 2.25-eV optical-absorption band and associated fluorescence at 1.36 eV. Studies of the polarization of the luminescence indicate a $\langle 110 \rangle$ orientation for the center. The Li_2^+ defect was chosen, not only because it could have the $\langle 110 \rangle$ symmetry, but also because the defect bleaches at temperatures at which Li^+ ions become mobile in the lattice and form metal aggregates. Mourad[13] has calculated the change in lattice energy of LiF upon introduction of this defect. Although the formation energy which he obtained (about 5.3 eV) is high, he found the defect to be stable. The calculated 4.0-a.u. internuclear separation means that the ion could readily be accommodated in the $\langle 110 \rangle$ orientation in LiF. However, since the excited-state relaxation of the ion is very small (which would be expected due to repulsion of nearest-neighbor Li^+ ions), the observed energy difference between the absorption energy (2.25 eV) and the emission energy (1.36 eV) cannot be accounted for on the basis of relaxation of an excited-state ion prior to emission. Furthermore, the polarization of the luminescence would suggest a $\Sigma \rightarrow \Sigma$ transition. We calculate that the only allowed dipole transition ($\Sigma_g \rightarrow \Sigma_u$) has an energy of 0.90 eV or less. No corresponding optical absorption is reported near this energy. In order to search for agreement between the experimentally observed optical transitions and calculations, it may be necessary to consider other defects or, for example, the alternative $\langle 121 \rangle$ orientation of the Li_2^+ ion.

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