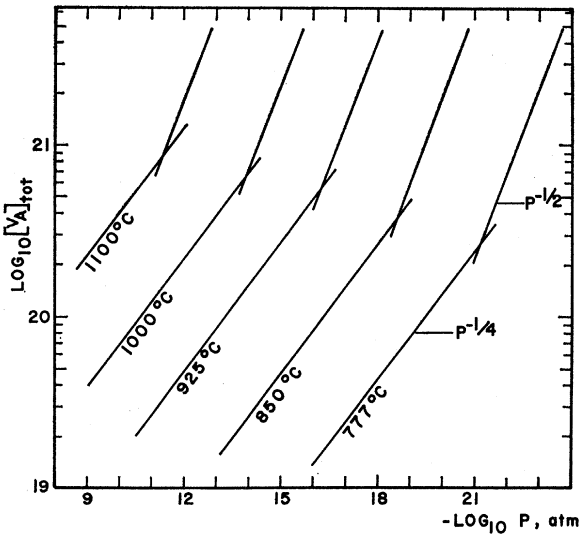


FIG. 3. Family of isotherms of oxygen-vacancy concentration calculated from the limiting forms of the solutions of Eqs. (25) and (26) at large X.

oxygen-vacancy defect model in this region and is very similar to that reported by Bevan and Kordis[18] for CeO_2. From this it appears to be possible to account for both the conductivity and gravimetric results for CeO_2 on the basis of an oxygen-vacancy model alone without making unreasonable assumptions regarding effective mass, dielectric constant, vacancy model, or vacancy-formation energies.

VI. DISCUSSION

The exact treatment of oxygen-vacancy defects in metal oxides may account, in some cases, at least, for the departure from a $P^{-1/4}$ or a $P^{-1/6}$ dependence without the necessity of introducing other defects such as cation interstitials. There are some experimental observations which would be in clear contradiction with the oxygen-vacancy model and a search for such contradictions may be the best way to proceed. For instance, a $P^{-1/5}$ dependence of conductivity over approximately ten orders of magnitude of oxygen partial pressure should rule out oxygen vacancies. The experiments on[2,7,17] Nb_2O_5 also seem to be clearly in contradiction with simple oxygen-vacancy defects. On the other hand, in the two cases where a $P^{-1/5}$ dependence of conductivity is observed,[1,3] there seem to be indications that the experiments could be located in the first intermediate region for oxygen vacancies. Also, if the gravimetric experiments on[18] CeO_2 do not involve serious departure from ideality, the transition from a $P^{-1/4}$ to a $P^{-1/2}$ dependence on oxygen partial pressure should represent a confirmation of the vacancy model. The cation interstitial defect should give a transition from $P^{-1/4}$ to $P^{-1/3}$.

PHYSICAL REVIEW VOLUME 133, NUMBER 5A 2 MARCH 1964

Electronic Structure of the M Center in LiCl and LiF*

AXEL MEYER AND R. F. WOOD
Solid State Division, Oak Ridge National Laboratory,† Oak Ridge, Tennessee
(Received 30 September 1963)

Experimental work of the past few years has fairly conclusively established that the M center in alkali halides consists of two F centers bound together at neighboring halide sites. Using this model, the wave functions and energy levels of the M center in LiCl and LiF are calculated in the Heitler-London approximation. The F-electron wave functions used in the calculations are of the vacancy-centered type. The finite extension of the neighboring alkali ions is treated but all other ions are considered to be point charges. The results of the calculations show that there is a transition energy which corresponds closely to the observed M_1 band. In addition, there are numerous possibilities for other transitions, all giving energies which cluster in the vicinity of the main F-band energy. The results for the M_1 band follow the empirical Ivey relationship quite well.

I. INTRODUCTION

OF the various models for the M center, the one proposed by van Doorn and Haven[1] has been the most successful in explaining the experimental data. According to this model, the M center consists of two F centers bound together at nearest-neighbor halide sites. Thus, the M center, in a sense, can be considered a lattice analog of the hydrogen molecule in free space. We shall sometimes refer to it as the F_2 molecule and speak of the F_2 model of the M center.

Very few theoretical calculations have been carried out on the M center, and, as far as we know, there have been no published results of detailed calculations based

* A preliminary report on this work was given in the Bull. Am. Phys. Soc. 8, 352 (1963).

† Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[1] C. Z. van Doorn and Y. Haven, Philips Res. Rept. 11, 479 (1956).

on the van Doorn-Haven model. Gourary and Luke[2] reported the results of calculations based on the model suggested by Seitz[3] which cast some doubt on its applicability to the M center. They obtained a transition energy which corresponds fairly closely to one of the observed M bands in a number of crystals; however, the variation of the energy of this transition with crystal does not agree at all well with the Ivey relation. Gourary and Luke obtained another transition energy which apparently has no relationship to any energy attributable to the M center. Later, we shall compare their results with those presented here.

A very important difference between the Seitz and the F_2 centers is that the former contains one electron, whereas the latter contains two. The unpaired electron of the Seitz model should have marked spin resonance properties which have not been observed experimentally. Of course, a two-electron model in a singlet ground state, because it has no unpaired electron, is not expected to show any spin-resonance effects. From the calculational standpoint, it is unfortunate that the F_2 model is apparently the appropriate one, since it is more difficult to treat a two-electron center than a single-electron one.

In this paper, we shall report on calculations which we have carried out on the F_2 model within the Heitler-London scheme. The calculations were done on LiCl and LiF because F-center wave functions of sufficient simplicity were available or could be obtained easily for these crystals. These functions are not the most accurate which we could have used, but evidently they do give a general idea of the true wave functions, and they predict F-center transition energies which correspond closely to those observed experimentally. Unfortunately, LiCl crystals are difficult to work with experimentally, and little or no data exist for them. LiF is a better crystal on which to attempt calculations, since more data are available for it than for LiCl. Crystals such as KCl, NaCl, which are preferred by experimentalists, are difficult to treat theoretically because of the complex electronic structure of the alkali ions.

In the next section, we shall give a discussion of the symmetry properties of the F_2 model and their relationships to the polarization properties of the absorbed light. Following that will be a section on the F-center wave functions which we have used. Next, we shall write down and discuss the M-center Hamiltonian and the Heitler-London-type wave functions. This discussion will be brief, since the theory is well known from the work on the hydrogen molecule.[4] In Sec. V, details of the calculations and the results will be given, and, in the final section, we shall discuss these results and some of their implications.

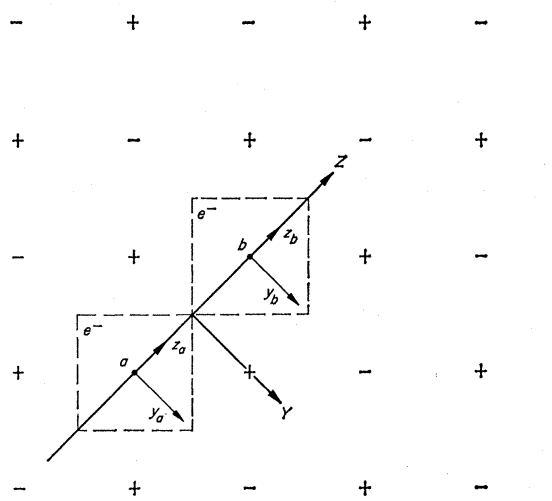


FIG. 1. Schematic representation of the F_2 model of the M center showing our choice of coordinate systems. The X, x_a, x_b axes are directed out of the plane of the figure.

II. SYMMETRY PROPERTIES OF THE M CENTER

The F_2 model of the M center is indicated in Fig. 1. Following the custom in molecular calculations, we take the Z axis along the line connecting the centers of the two vacancies. If we were to consider the crystal as a continuous medium in which the F_2 molecule is imbedded, we would have to deal with the $D_{\infty h}$ symmetry group in complete analogy with homonuclear diatomic molecules, and, indeed, rough calculations have been made on the F_2 model with this approach.[5] Here, however, we want to take into account explicitly the ionic properties of the crystal surrounding the F_2 molecule. An examination of this case in an alkali halide crystal shows that the D_{2h} group is the appropriate one. This group has eight irreducible representations denoted in molecular notation by A_{1g}, A_{1u}; B_{1g}, B_{1u}; B_{2g}, B_{2u}; B_{3g}, B_{3u}. The three components of the dipole moment operator transform according to the B's, and they are chosen here so that X, Y, Z transform according to B_{3u}, B_{2u}, and B_{1u}, respectively, with our choice of coordinate system. Also, since X, Y, Z change sign under inversion, optical transitions can go only from g to u states. We have calculated energies going with all of the above representations except A_{1u}.

We have chosen our Z axis along a $\langle 110 \rangle$ direction. The above results then show that light polarized with its electric vector in this direction will produce the transition $A_{1g} \rightarrow B_{1u}$. Light polarized in the Y and X directions will produce transitions to the B_{2u} and B_{3u} levels. It should be noted that the Y axis is also in a $\langle 110 \rangle$ direction, but that the X axis is in a $\langle 100 \rangle$ direction. From his experimental work on KCl, Okamoto[6] has identified six bands which are presumably associated with the M center. He labels these the M_1, M_2,

[2] B. S. Gourary and P. J. Luke, Phys. Rev. **107**, 960 (1957).
[3] F. Seitz, Rev. Mod. Phys. **18**, 384 (1946).
[4] See, for example, J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. 1, Chap. 3.
[5] C. Z. van Doorn, Philips Res. Rept. Suppl. 4 (1962).
[6] F. Okamoto, Phys. Rev. **124**, 1090 (1961).

M_3, M_4, M_2', M_3' bands. The occurrence of the primes on the last two letters is supposed to indicate that these bands are very closely related to the ones denoted by the corresponding unprimed letter. For the sake of clarity, we shall anticipate our results by stating that our transition $A_{1g} \rightarrow B_{1u}$, very probably, is the one giving rise to the band which Okamoto labels M_1. We shall, sometimes, follow Okamoto's terminology for this band. The M_1 band is the one which is usually referred to simply as the M band. Okamoto found that his M_2 and M_2' bands lie just under the F band and are separated by about 0.03 eV from each other. The transitions which are responsible for these bands are not obvious from our calculations, and so we shall not follow Okamoto's terminology here. Instead, we shall label the band with the same symbol used for the excited state involved in the transition.

III. THE F-CENTER WAVE FUNCTIONS

For the F-center wave functions, we have used those of the type employed by Wood and Korringa,[7] with some modifications. These authors found that a simple $2s$ function of the Slater type for the ground state and a $3p$ function for the first excited state gave quite accurate results for the transition energy corresponding to the F band in LiCl. However, they found that a $2p$ function is also a fairly good approximation to the excited state. In order to take advantage of the extensive literature[8] available on the calculation of molecular integrals, we have chosen to use the $2p$ function.

The original calculations of Wood and Korringa on LiCl did not include the exchange energy of the F-center electron with the neighboring lithium cores. This has now been included, but the distortions of the lattice in the neighborhood of the defect have been neglected. The effective Hamiltonian of the F-center electron in the crystal is taken to be

$$H_F = H_1 + H_2 + H_3, \tag{1}$$

where

$$H_1 = -\tfrac{1}{2}\nabla^2, \tag{2}$$

$$H_2 = -\sum_{\nu=1}^{N-1} \frac{Z_\nu}{|\mathbf{r}-\mathbf{R}_\nu|} + 2\sum_{\nu,j} \int \frac{\phi_{\nu j}^2(\mathbf{r}')d\tau'}{|\mathbf{r}-\mathbf{r}'|}, \tag{3}$$

and

$$H_3 = -\sum_{\nu,j} \int \frac{\psi(\mathbf{r}')\phi_{\nu j}(\mathbf{r}')d\tau'}{|\mathbf{r}-\mathbf{r}'|} \frac{\phi_{\nu j}(\mathbf{r})}{\psi(\mathbf{r})}. \tag{4}$$

In these expressions, ψ is the wave function of the F electron, which is associated with a vacancy at the ion site given by $\nu=0$, and $\phi_{\nu j}$ is the jth atomic orbital on the νth ion. The 2 before the second integral in Eq. (3) is the usual spin factor. We have included the effects of the finite size of the ions and of exchange only for the nearest-neighbor Li ions. For more distant ions, H_3 vanishes and the two terms in H_2 combine to give just the potential due to a point ion.

The ground-state, F-center wave function is

$$\psi = N_F[\phi_{2s}(\mathbf{r}) + \sum_\nu c_\nu \phi_\nu(\mathbf{r}-\mathbf{R}_\nu)] \tag{5}$$

in which

$$\phi_{2s}(\mathbf{r}) = (\beta^5/3\pi)^{1/2} r e^{-\beta r}, \tag{6}$$

$$\phi_\nu(\mathbf{r}) = (2.69^3/\pi)^{1/2} e^{-2.69r}. \tag{7}$$

The c's are determined by the orthogonality condition,

$$\langle \psi | \phi_\nu \rangle = 0, \tag{8}$$

and are assumed to be zero for the ϕ's on sites more distant than nearest neighbors. The excited-state wave functions are given by

$$\psi' = N_F'[\phi_{2p}(\mathbf{r}) + \sum_\nu c_\nu' \phi_\nu(\mathbf{r}-\mathbf{R}_\nu)] \tag{9}$$

in which

$$\begin{aligned} \phi_{2pz}(\mathbf{r}) &= (\gamma^5/\pi)^{1/2} r e^{-\gamma r} \cos\theta, \\ \phi_{2px}(\mathbf{r}) &= (\gamma^5/\pi)^{1/2} r e^{-\gamma r} \sin\theta \cos\phi, \\ \phi_{2py}(\mathbf{r}) &= (\gamma^5/\pi)^{1/2} r e^{-\gamma r} \sin\theta \sin\phi. \end{aligned} \tag{10}$$

In LiCl, the ground-state energy is minimized at a value of -0.2064 a.u. for $\beta=0.75$ and the excited state at a value of -0.0850 a.u. for $\gamma=0.49$. The corresponding numbers for LiF are -0.2112 a.u. at $\beta=0.94$ for the ground state and -0.0361 a.u. at $\gamma=0.57$ for the excited state. It is interesting to note that the difference in the transition energies in LiCl and LiF is due almost entirely to the large difference in the energy of the excited states in the two crystals.

IV. THE HAMILTONIAN AND WAVE FUNCTIONS OF THE M CENTER

For the Hamiltonian of the M-center problem, we take

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 + \sum_{\substack{\nu=1 \\ \nu\neq a,b}}^{N} [V_\nu(\mathbf{r}_1-\mathbf{R}_\nu) + V_\nu(\mathbf{r}_2-\mathbf{R}_\nu)] + r_{12}^{-1} + R_{ab}^{-1} \tag{11}$$

in which ν runs over all of the ions in the crystal, except the two which are missing at sites a and b in Fig. 1. The numbering scheme here differs slightly from that in Eqs. (2)–(4) for obvious reasons. The subscripts a and b can also be taken to indicate the vacancies and the term R_{ab}^{-1} is the energy of interaction between two vacancies in an otherwise perfect alkali halide crystal. We have taken this to be simple Coulombic, which may not be exactly correct. In any case, the term drops out when calculating transition energies. We take the potential V_ν to correspond to the same approximation used in

[7] R. F. Wood and J. Korringa, Phys. Rev. **123**, 1138 (1961).

[8] M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen Company, Ltd., Tokyo, 1955); J. Miller, J. M. Gerhauser, and F. A. Matsen, *Quantum Chemistry Integrals and Tables* (University of Texas Press, Austin, 1958).

the F-center problem so that we can introduce the effective Hamiltonian of Eq. (1) when it is convenient to do so.

We have chosen our wave functions to be of the Heitler-London form. For example, in the singlet ground state, we take

$$\Psi(12)=N[\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)], \quad (12)$$

where ψ_a and ψ_b are the normalized F-center wave functions at the a and b vacancies. N is a normalization factor. The normalized singlet spin functions are given by

$$\theta(12)=(1/\sqrt{2})[\alpha(1)\beta(2)-\alpha(2)\beta(1)]. \quad (13)$$

We have not calculated the triplet states at all.

Following the standard calculation of this type on the hydrogen molecule, we write

$$E_{Mg}=\langle\Psi|H|\Psi\rangle=2N^2[J+K] \quad (14)$$

and

$$J=\langle\psi_a(1)\psi_b(2)|H|\psi_a(1)\psi_b(2)\rangle, \quad (15)$$

$$K=\langle\psi_a(1)\psi_b(2)|H|\psi_a(2)\psi_b(1)\rangle. \quad (16)$$

When we consider J, we regroup the terms in the Hamiltonian and write

$$H=H_{Fa}(1)+H_{Fb}(2)-V_b(\mathbf{r}_1-\mathbf{R}_b)-V_a(\mathbf{r}_2-\mathbf{R}_a)+r_{12}^{-1}+R_{ab}^{-1}. \quad (17)$$

Here $H_{Fa}(1)$ and $H_{Fb}(2)$ are the appropriate Hamiltonians for the isolated F centers at a and b [Eqs. (1)–(4)]. We find then that

$$J=2E_{Fg}-2\langle\psi_a(1)|V_b(\mathbf{r}_1-\mathbf{R}_b)|\psi_a(1)\rangle+\langle\psi_a(1)\psi_b(2)|r_{12}^{-1}|\psi_a(1)\psi_b(2)\rangle+R_{ab}^{-1}. \quad (18)$$

E_{Fg} is the energy of an F center in its ground state. Since H is symmetric in 1 and 2, we interchange them in Eq. (17) and get for K

$$K=2\langle\psi_a(1)|H_{Fb}|\psi_b(1)\rangle S_{ab}-2\langle\psi_a(1)|V_b(1)|\psi_b(1)\rangle S_{ab}+\langle\psi_a(1)\psi_b(2)|r_{12}^{-1}|\psi_b(1)\psi_a(2)\rangle+S_{ab}^2R_{ab}^{-1}. \quad (19)$$

Here,

$$S_{ab}=\langle\psi_a|\psi_b\rangle. \quad (20)$$

We tried making the approximation that

$$\langle\psi_a|H_{Fb}|\psi_b\rangle=E_{Fg}\langle\psi_a|\psi_b\rangle \quad (21)$$

but found it inadequate. The exact calculation of the left-hand side of Eq. (21) is made difficult by the occurrence of three center integrals. We shall discuss this further in the next section.

Denoting the second and third terms in Eq. (18) by J_1 and J_2, and the corresponding terms in Eq. (19) by K_1 and K_2, we obtain for the energy of the M-center ground state

$$E_{Mg}=4N^2[E_{Fg}+\langle\psi_a|H_{Fb}|\psi_b\rangle S_{ab}-J_1-K_1+\tfrac{1}{2}(J_2+K_2)]+R_{ab}^{-1}. \quad (22)$$

The binding energy of the M center we take to be

$$B_{Mg}=E_{Mg}-2E_{Fg}. \quad (23)$$

For the ungerade singlet excited states we have a somewhat more complicated wave function, namely,

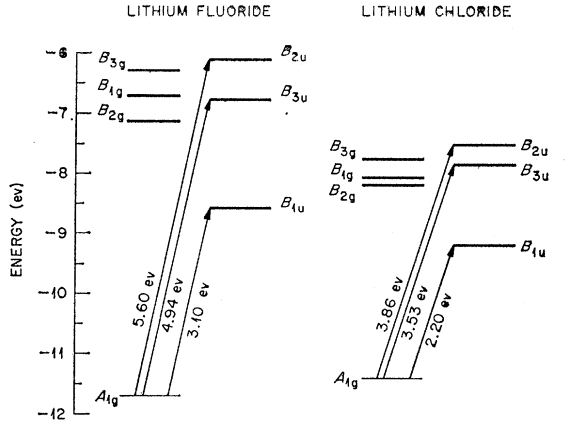
$$\Psi'(12)=N'[\psi_a(1)\psi_b'(2)+\psi_a(2)\psi_b'(1)+\psi_a'(1)\psi_b(2)+\psi_a'(2)\psi_b(1)], \quad (24)$$

where the prime on Ψ indicates one of the three excited state functions of the M center obtained by substituting in one of the functions given by Eqs. (9) and (10). One can see directly now that the threefold degenerate first excited state of the F center gives rise to the B_{1u}, B_{2u}, and B_{3u} levels of the M center in the Heitler-London approximation. Gerade functions can be obtained from Eq. (24) by changing the signs of the last two terms. However, the B_{1g} function, unlike the others, is not automatically orthogonal to the ground state, and this complicates the energy calculations somewhat.

V. DETAILS OF CALCULATIONS AND RESULTS

When the functions given by Eqs. (5) and (12) are inserted in Eqs. (18) and (19), some rather complicated expressions result. The only really difficult problems arise, however, from the calculation of the integrals. Because of our choice of F-center functions, most of the one- and two-electron, and one- and two-center integrals can be calculated with the aid of various sets of tables which appear in the literature.[8] Three-center integrals also occur occasionally, but most of these can be approximated quite accurately. Important in this connection is the very compact nature of the Li^+ function and the extensive nature of the ϕ_{2s} and ϕ_{2p} functions. This allows one to argue that the ϕ_{2s} and ϕ_{2p} functions are practically constant over the volume in which the Li^+ functions have appreciable value and to bring them outside of the integral sign. Other integrals which we have been forced to approximate are some of the two-center, two-electron Coulomb and exchange integrals involving $2p\pi$ functions, that is, $2p$ functions which have their principal symmetry axes perpendicular to the line joining the two coordinate origins. Fortunately, these integrals are small and tend to cancel each other. The integrals have been approximated in a number of different ways with good agreement.

In dealing with $\langle\psi_a|H_{Fb}|\psi_b\rangle$ of Eq. (19), we made the following approximations. To H_{Fb}, we added and subtracted a term due to the missing ion at site b so that we obtained the potential due to a perfect crystal minus the potential due to a halide ion at b. We then observed that, in a region midway between two second nearest-neighbor ions in a perfect alkali halide crystal, the potential is very nearly zero and that for a spherical charge distribution centered at the midpoint of the line connecting the two vacancies, the positive and negative variations in potential tend to cancel each other. We then set that part of the energy due to the perfect crystal potential



Energy Level Diagrams of M Centers Showing Absorption Band Energies.

FIG. 2. Energy-level diagrams for the M centers in LiF and LiCl. Transitions are forbidden between the gerade levels in a rigid, undistorted crystal but may be partially allowed in a real crystal.

equal to zero in $\langle\psi_a|H_{Fb}|\psi_b\rangle$ and calculated the kinetic energy and the potential energy in the field of the subtracted halide ion, treated as a point charge, at b. We feel that this is a fairly good approximation as long as the overlap charge density is almost spherically symmetric and is centered near the midpoint of the line joining the two vacancies. The dominating role of the potential due to the subtracted halide ion should be kept in mind here.

When the energy expressions for each of the levels are obtained, it is interesting to note that the B_{2u} and B_{3u} levels would be degenerate in our approximation if it were not for the orthogonalization to the ion cores given by Eqs. (5) and (9). This orthogonalization produces a separation of the energies of the two states in qualitative agreement with experimental results, which is one of the promising features of the calculations.

In carrying out the calculations on LiCl, we allowed the variation parameters in the F-center functions to vary in the M-center calculation. In this way, we established that the values of the parameters which minimize the F-center energies are very nearly the same as the values which minimize the M-center energies. This is in contrast to the hydrogen molecule, where a small variation in the atomic screening parameter results in a marked lowering of the ground-state energy. We did not repeat the calculation in as much detail for LiF.

There is a further point which is of interest and which greatly simplifies the calculations. The parameters which are important in the one- and two-electron, two-center integrals are the products of the F-center variation parameters and the intervacancy distances. With the values given above and the intervacancy distances, R_2, of 6.873 a.u. for LiCl and 5.374 a.u. in LiF, we find that

$$\beta R_2(\text{LiCl})=5.155;\quad \beta R_2(\text{LiF})=5.048,$$
$$\gamma R_2(\text{LiCl})=3.368;\quad \gamma R_2(\text{LiF})=3.063.$$

TABLE I. Total electronic, binding, and transition energies of various singlet states of the M center (energies are given in eV).

	Lithium fluoride			Lithium chloride		
State	Energy	Binding energy	Transition energy	Energy	Binding energy	Transition energy
A_{1g}	−11.70	−0.21		−11.40	−0.16	
B_{1u}	−8.60	−1.91	3.10	−9.20	−1.27	2.20
B_{1g}	−6.70	−0.01		−8.08	−0.15	
B_{2u}	−6.10	+0.59	5.60	−7.53	+0.40	3.86
B_{2g}	−7.13	−0.43		−8.19	−0.25	
B_{3u}	−6.76	−0.07	4.94	−7.86	+0.07	3.53
B_{3g}	−6.28	+0.41		−7.77	+0.17	

These values are not exactly equal, but we have found that the energies of the ground and excited states in LiCl have rather shallow minima. Therefore, we have used the same values of βR_2 and γR_2 for both LiCl and LiF, namely, $\beta R_2=5.00$ and $\gamma R_2=3.25$. This allows us to make a simple change of scale of those parts of the energy which depend on βR_2 and γR_2. We then have only to apply corrections due to the orthogonalization of the F-center wave functions to the neighboring Li cores. These corrections are considerably different in the two crystals.

Aside from the actual energies, other quantities of interest are the binding energies in the various states. We use binding energy here in the sense of Eq. (23), i.e., it is the difference in the energy of two F centers, at infinite separation in a perfect crystal, and the M-center energy. This definition is clear for the ground state, but we shall also speak of a binding energy of the M center when it is in an excited state. In this case, we are referring the energy of the excited M center to two infinitely separated F centers, one of which is in an excited state. Thus,

$$B_{Me}=E_{Me}-E_{Fg}-E_{Fe}. \tag{25}$$

The results of our calculations are shown in Table I, and they are compared to the available experimental data in Table II. In Fig. 2 we have displayed most of the data in Table I on an energy level diagram. Finally, in Fig. 3, we show graphically some of the experimental and theoretical results on the F- and M-center transition energies in the alkali halides. The solid lines are obtained from the empirically derived Ivey[9] equa-

TABLE II. The energies of the various bands from theory and experiment. All energies are in eV. There are no experimental values for the other bands. We use the ∼ sign because there are small variations in the experimental values which have been reported.

	F Band			M_1 Band (B_{1u})		
Crystal	Theory	Exptl.	Percent error	Theor	Exptl.	Percent error
LiF	4.76	∼4.96	∼4.0	3.10	∼2.79	∼11.1
LiCl	3.29	∼3.15	∼4.5	2.20	∼1.9	∼15.8

[9] H. F. Ivey, Phys. Rev. 72, 341 (1947).

tion for the M center and the very similar equation used by Smakula[10] for the F center. This last relationship differs somewhat from the Ivey equation for F centers because Smakula has used slightly different parameters for the different alkalis in an effort to obtain better agreement with the data than that obtained by Ivey. The dashed lines are those obtained by Gourary and Luke for their calculations based on the old Seitz model. Experimental values are indicated by dots and our theoretical values by triangles and circles.

VI. DISCUSSION

Experimental results on the F and M bands in LiF and, particularly, in LiCl are sparse at this time. Therefore, the comparisons of our results with experimental data must be of an approximate nature.

From Table II it can be seen that the calculated F-transition energy for LiCl is too high by about 5%. In LiF the agreement with experiment is comparably good for the F band. It is well known that the prediction of a transition energy is not a severe test for wave functions since errors in the energies of the two states involved usually tend to cancel each other. A more sensitive indicator of the correctness of the F-center wave functions (at least at particular places in the crystal) is the contact term of the hyperfine interaction. The ground-state wave functions used here for the F center give values of the hyperfine interaction with the nearest-neighbor Li^+ ions which are too high by a factor of 2 to 3. Thus, we conclude that these wave functions are somewhat inaccurate in detail but probably give a reasonable indication of the over-all charge distribution.

Among the factors which contribute to the failure of our functions to duplicate the detailed features of the exact F-center wave functions, the only one which we want to discuss here is the lack of adequate treatment of the higher order angular momentum components. The function ϕ_{2s} in Eq. (5) is spherically symmetric. An analysis of the potential appropriate to the F-center problem[11] indicates that the spherical approximation is not adequate. Some higher order angular momentum terms are incorporated in the wave function by the orthogonalization to the ion core orbitals, but it is unlikely that this procedure compensates in the exactly correct way for the inadequacy.

The defects of the F-center wave functions and the lack of flexibility of the simple Heitler-London approach make it unreasonable to expect close agreement with experimental results. Therefore, the ~13% disagreement with the experimental data on the M_1 line in our two crystals is not at all surprising. The fact that, as Fig. 2 indicates, the slope of our line is nearly the same as the slope of the line given by the Ivey relationship is encouraging. This is in contrast to the "M_1" line obtained by Gourary and Luke on the basis of the Seitz model.

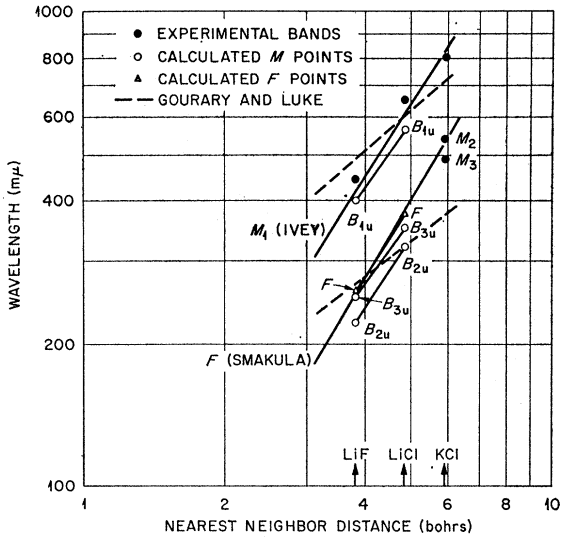


FIG. 3. Variation of transition wavelengths with lattice parameter. The Gourary and Luke lines are based on the old Seitz (Ref. 3) model. The experimental data on KCl were taken at liquid-nitrogen temperature (Ref. 6). All other data are appropriate at room temperature.

The experimental data on the other bands is very meager. As was mentioned earlier, Okamoto found that, in KCl, two of these bands, which he labels M_2 and M_2', lie just under the F band and that they are separated from each other by about 0.03 eV. They have symmetry properties corresponding to our B_{2u} and B_{3u} levels, respectively, and the M_2 band lies at the lower energy. We note, however, that Okamoto's M_3 band is separated from his M_2 band by about 0.26 of an electron volt. These separations were determined by polarized light techniques which showed that the M_2 and M_3 bands have similar polarization properties. Our energy-level diagram shows the B_{3u} level lying lower than the B_{2u}, contrary to Okamoto's results on the M_2 and M_2' bands. Our splittings are rather large and do not compare well with Okamoto's M_2-M_2' splitting. However, our B_{3u} and B_{2u} levels do correlate well in energy and symmetry with Okamoto's M_2' and M_3 bands, respectively. Recent work by Kaufman and Clark[12] on LiF has shown the presence of two bands at 5.390 and 5.548 eV, one or both of which might conceivably be associated with the B_{2u} and B_{3u} levels.

The origin of the splitting between the B_{2u} and B_{3u} levels in our calculations makes it at least plausible to expect a greater effect in the lithium halides than in the other alkali halides. This is primarily because of the high energy of the Li^+ 1s orbitals which are introduced by the orthogonalization procedure. The orbitals playing the corresponding role in the other alkali halides do not

[10] See, for example, A. Smakula, N. C. Maynard, and A. Repucci, Phys. Rev. **130**, 113 (1963).
[11] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).
[12] J. V. R. Kaufman and C. D. Clark, J. Chem. Phys. **38**, 1388 (1962).

have nearly so great an energy associated with them. On the other hand, one should remember that the calculation of the hyperfine interaction indicates that the wave functions have too much Li^+ $1s$ orbital mixed in. This might tend to make the calculated separation of the B_{2u} and B_{3u} levels too large, just as it makes the calculated value of the hyperfine interaction too large. One would need to know the correct admixture of the core orbitals, as well as their energy, in order to make quantitative statements about the splitting. In summary, then, we expect the separation to be larger in the lithium halides, particularly in LiF, than in other crystals, but we also expect that our calculations may overestimate the separation somewhat. We must leave open, then, except in the case of the M_1 band, the problem of setting up correspondences between our levels and Okamoto's bands. We note that the excited gerade levels lie near the B_{2u} and B_{3u} levels. In a rigid lattice, transitions from the A_{1g} level to these excited gerade levels will be forbidden, but this may no longer be true in a real vibrating crystal. This introduces further complications into the problem of interpretation.

Figure 2 shows that the slopes of B_{2u} and B_{3u} lines are approximately the same as that of the F line. That the B_{2u} and B_{3u} lines should be closely related, energetically, to the F band can be understood from the calculations. The wave functions for the excited states going with these two levels are made up of a correctly symmetrized combination of a $2s$ function at one vacancy and a $2p$ function, with its principal symmetry axis perpendicular to the line connecting the vacancies, at the other vacancy. With this arrangement the overlap of the F-center wave functions and the interaction of the two charge clouds is much less than it is when the symmetry axis of the $2p$ functions coincides with the line connecting the vacancies, as in the case of the B_{1u} state. This is indicated clearly in Table I, which shows the binding energy. Because this energy is smaller in the B_{2u} and B_{3u} states than in the B_{1u} state, the B_{2u} and B_{3u} lines lie closer to the F line than does the B_{1u} line.

Van Doorn[13] has estimated the ground-state binding energy of the two F centers which, evidently, make up the M center to be about 0.4 eV in KCl. We know of no estimates for LiCl or LiF, but it is to be expected that they would be about the same magnitude. Our values of 0.16 eV for LiCl and 0.21 eV for LiF appear to be reasonable. It is interesting to note that the binding energy, as we have defined it, is considerably greater in the B_{1u} state than in any other state. We feel that this may be of significance in the explanation of the formation of M centers from F centers.

As we have seen, Okamoto's work on the M center in KCl has shown that there are many bands which are related to the center. The K band has long been considered to be due to an excited state of the F center, and Lüty[14] has established the existence of other bands which he attributes to still higher excited states. Wood,[15] from theoretical calculations on LiCl, has found excited levels of the F center which tend to confirm Lüty's interpretation, at least qualitatively. It seems reasonable to us, then, to attribute at least some of Okamoto's additional lines to excited states of the M center which are related to the excited levels of the F center in much the same way as the B_{1u}, B_{2u}, and B_{3u} levels in this calculation are related to the first excited level of the F center. When we consider this and the possibility mentioned above that transitions to gerade excited states may not be absolutely fobidden in a real crystal, we see that it is not difficult to understand the origin of the many lines. We actually seem to have a plethora of possibilities.

Improvements in these calculations could be made by using better F-center wave functions and then incorporating some, or all, of the methods which have been applied to the hydrogen molecule, such as inclusion of ionic terms, hybridization, configuration interaction, etc. In spite of the crudeness of our starting wave functions, we feel justified in concluding, from our results and the discussion given above, that the F_2 model of the M center is on a sound theoretical, as well as experimental, basis.

ACKNOWLEDGMENTS

We are very grateful to H. W. Joy, who has programmed the CDC1604 for the calculation of a number of the more difficult integrals. We also wish to thank H. C. Schweinler and other members of the Solid State Division of the Oak Ridge National Laboratory for their constructive comments.

[13] See Ref. 5, p. 75.

[14] F. Lüty, Z. Physik **160**, 1 (1960).

[15] R. F. Wood, Phys. Rev. Letters **11**, 202 (1963).