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PHYSICAL REVIEW B VOLUME 3, NUMBER 11 1 JUNE 1971

Molecular-Orbital Model for KCl : Tl

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(Received 31 March 1970; revised manuscript received 4 January 1971)

A semiempirical molecular-orbital calculation is developed for describing the energy levels of KCl : Tl. This approach is conceptually more satisfactory than the ionic one, as the nature of a Tl-Cl bond is largely covalent. The computations are first carried out in the one-electron approximation, and then the Coulomb and spin-orbit interactions are taken into account. No attempt is made at an exact calculation, but it is demonstrated that the covalent calculation gives a consistent interpretation of the absorption spectrum.

I. INTRODUCTION

The absorption spectrum characteristic of Tl^+ in alkali halide crystals consists of four bands labeled *A*, *B*, *C*, and *D*. The *A*, *C*, and *D* bands are strong and rather temperature independent, whereas the strength of the weaker *B* band is temperature dependent. The *A*, *B*, and *C* bands arise from transitions to excited states of the activator, whereas the *D* band is due to excited states of the host crystal (perturbed excitons).[1,2] The *A*, *B*, and *C* bands are qualitatively explained by the model proposed by Seitz,[3] and quantitative approaches to the problem of determining them were taken by Williams[4] on the basis of the ionic model. However, it was suggested[5,6] that a purely ionic description of the luminescence center was erroneous, and that modifications would have to be made to obtain accurate results. Subsequently, Sugano[7] proposed the use of the molecular orbitals in order to explain the A, B, and C absorption bands. Starting from this framework, he obtained the right value for the ratio of the C-band dipole strength to the A-band dipole strength. However, it is easily shown that the Sugano formula is independent of the representation and can be also derived using a vacancy-centered model.

The positions of the A, B, and C bands are described by three parameters: W_0, G, ζ. The quantity W_0 is the energy difference between the first-excited-state and the ground-state configuration, whereas G and ζ are the exchange and spin-orbit energies, respectively. One of the salient features of the alkali halide environment is the considerable reduction in all of these quantities in the solid with respect to the free-ion values.[8]

In this paper the absorption spectrum of Tl^+ in alkali halides is discussed within a molecular-orbital framework; this approach is conceptually more satisfactory than the ionic one, as the nature of the Tl-Cl bond is largely covalent.[9]

In Sec. II the energy levels of the luminescence center are evaluated in the one-electron approximation using an extended Hückel theory. In Sec. III the Coulomb and spin-orbit interactions are taken into account, and in Sec. IV a comparison with the experimental data is presented.

Though no attempt is made at an exact calculation, it is demonstrated that the covalent calculation gives a consistent interpretation of the absorption spectrum.

II. MOLECULAR-ORBITAL THEORY

As is well known, in KCl : Tl the Tl^+ ions constitute the luminescence centers, each of these being surrounded by six Cl^- ions disposed according to O_h symmetry.[3] In the purely ionic picture[4] one studies the external electrons of the central atom under the influence of the crystal potential created by the neighboring chlorines (and also by ions further removed). The molecular-orbital (MO) model treats the $(TlCl_6)^{5-}$ complex as a single molecule. Moreover, the effect arising because the complex is embedded in a crystal must be taken into account.

The molecular-orbital method in its linear combination of atomic orbitals (LCAO) form is employed.[10] We assume that the nonvalence shell electrons of thallium and chlorines are unaffected by the bonding and that the Tl and Cl nuclei plus these inner-shell electrons form an effective core into the field of which the valence electrons are to be placed. Thus, we consider only the $6s$ and $6p$ atomic orbitals of the central atom and only the $3p$ atomic orbitals of the chlorine atoms[11] in constructing the molecular orbitals. We do not consider the effect of higher-lying metal orbitals ($6d$, etc.) as their energies are not suitable for bonding. In the case of the complex here discussed, 36 electrons from the ligands and 2 electrons from Tl^+ are to be placed in the molecular orbitals, the ground state being constructed by placing 38 electrons in the lowest-lying molecular orbitals.

The Hamiltonian of the system can be written as follows:

$$\mathcal{H} = \sum_k h_k + \sum_{k>l} \frac{e^2}{r_{kl}} + H_{so} + V_c \ ,$$

where h_k is the Hamiltonian for the kth valence electron moving in the field of atomic cores considered in fixed positions (adiabatic approximation), the second and third term on the right-hand side represent the Coulomb and spin-orbit interactions and V_c represents the effect arising because the molecule is embedded in a crystal.

The computation of the molecular parameters may be carried out by the self-consistent field method.[12] Because of the great complexity of this method, we have used the extended Hückel theory.[10,11,13]

Here, the true Hamiltonian is replaced by a sum of one-electron Hamiltonians H that contains both the kinetic energy of the electron and its electrostatic interaction with the field of the atomic cores and the averaged field of the remaining valence electrons.

The one-electron molecular orbitals are of the form $\Psi(\Gamma) = c_1\varphi_M + c_2\sum_i a_i\varphi_i$, where φ_M is a wave function of the central atom, transforming in the molecular point group as the irreducible representation Γ, and $\sum_i a_i\varphi_i$ is a linear combination of ligand wave functions transforming as the same irreducible representation. In the case of O_h symmetry, the proper set of ligand basis functions and their metal ion counterparts are given in Ref. 10. The coordinate system used is shown in Fig. 1. The one-electron molecular orbitals to be considered here are

$$\Psi_\sigma(a_{1g}) = c_1(6s) + \left(\frac{c_2}{\sqrt{6}\,\lambda_2}\right) \sum_{k=1}^{6} z_k \ ,$$

$$\Psi_{\sigma,\pi}(t_{1u,x}) = c_1(6p_x) + \left(\frac{c_2}{\sqrt{2}\,\lambda_2}\right) (z_1 - z_4) + \left(\frac{c_3}{2\lambda_3}\right) (x_3 + y_2 - x_5 - y_6) \ ,$$

$$\Psi_{\sigma,\pi}(t_{1u,y}) = c_1(6p_y) + \left(\frac{c_2}{\sqrt{2}\,\lambda_2}\right) (z_2 - z_5) + \left(\frac{c_3}{2\lambda_3}\right) (x_1 + y_3 - x_6 - y_4) \ ,$$

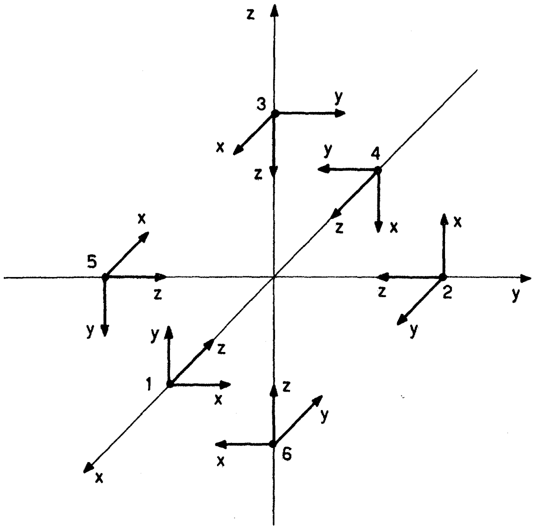

FIG. 1. Coordinate system and numbering used in the MO calculation.

$$\Psi_{\sigma,\pi}(t_{1u,z}) = c_1(6p_z) + \left(\frac{c_2}{\sqrt{2}\,\lambda_2}\right)(z_3 - z_6) + \left(\frac{c_3}{2\lambda_3}\right)(x_2 + y_1 - x_4 - y_5) \,, \tag{1}$$

where x, y, z refer to $3p_x$, $3p_y$, $3p_z$ chlorine orbitals, respectively. The effect of the overlap of the ligands with themselves has been taken into account by the inclusion of constants λ in Eqs. (1).[11] In our case the t_{2g}, t_{2u}, t_{1g}, and e_g are nonbonding orbitals and their energy levels are equal to those of $3p_{\pi,\sigma}$ and $3p_\sigma$ chlorine orbitals, respectively.

For each molecular orbital the averaged energy $(H)_{av}$ is calculated and the coefficients c_i are varied so that $\delta(H)_{av} = 0$. This leads to a system of linear equations $\sum_i c_i(H_{ij} - G_{ij}E) = 0$ from which the c_i are evaluated. The condition that these equations are soluble provides the secular equation $|H_{ij} - G_{ij}E| = 0$ from which the energy levels E are obtained. In our case we have to solve only a second- and a third-degree equation for a_{1g} and t_{1u} levels, respectively. In order to solve for the energy levels, three quantities must be evaluated: G_{ij}, H_{ii}, and H_{ij}.

Hartree's numerical values[14] of Cl^- and Tl^+ radial functions were used for our computations. The numerical values of $R(r)$ were fitted with analytical functions as follows:

$$\begin{aligned} R_{3p}(r) &= r^2(4.96e^{-2.2r} + 0.156e^{-r}), \\ R_{6s}(r) &= 0.699r^3e^{-1.5r} \,, \\ R_{6p}(r) &= 0.256r^3e^{-1.2r} \,. \end{aligned} \tag{2}$$

The overlap integrals G_{ij} were then evaluated in the usual way.[15]

For $6s$ and $6p$ orbitals the diagonal H_{ii} terms are estimated as the sum of ionization potentials V_i plus the Madelung energy E_M, that is, $-H_{ii} = V_i + E_M$. In calculating E_M we have taken into account the effective charges of Tl and Cl ions.[16] (The quantity E_M in KCl is $Ae^2/R = 8$ eV, where [17]$A = 1.75$ and $R = 5.95$ a.u. is the internuclear distance.[18])

Since single-electron ionization potentials and Madelung energy are functions of the metal charge q it was necessary to iterate the computation until the H_{ii} terms taken were appropriate for the final charge distribution and the electronic configuration calculated for the complex. The quantities V_i for various electronic configurations of integral charge were obtained from Moore's table of atomic spectra.[19] They are obtained as a difference of the weighted mean of the energies of the terms arising from the final and starting electronic configurations. The weighting factor is equal to the total degeneracy of the term.[20] Curves of ionization energy as a function of charge on Tl for various electronic configurations were interpolated for fractional charge on Tl (Fig. 2). The charge q is allowed to vary from 0 to 1 a.u.

To evaluate V_i for an arbitrary charge configuration, the configuration is represented as a linear combination of the configurations for which the V_i curves have been set up; V_i is then taken as the same linear combination of the respective V_i's.[21] $(V_i)_{6s}$ and $(V_i)_{6p}$ were then evaluated starting from the formulas

$$(V_i)_{6s} = V_i(6s^2 6p^{1-q}) \,,$$

$$(V_i)_{6p} = (1+q)V_i(6s^{2-q}6p) - qV_i(6s^{1-q}6p^2).$$

Similarly, the ligand H_{ii}'s are made self-consistent taking into account their effective charge which is allowed to vary from -0.833 to -1 (see Fig. 3). Moreover, in evaluating the H_{ii} terms, the corrections due to ligand-ligand overlap has been taken into account.[22] The quantity V_i for the ligands is interpolated between the electron affinity A_e of Cl^0 ($A_e = 3.82$ eV [23]) and V_i of Cl^0 ($V_i = 13.01$ eV [19]).

For the off-diagonal terms H_{ij}, we have made use of the Wolfsberg-Helmholtz approximation[24] which is $H_{ij} = \frac{1}{2}k(H_{ii} + H_{jj})G_{ij}$, where, the value of 1.75 for the constant k was assumed.

The secular equations $|H_{ij} - G_{ij}E| = 0$ are solved as follows: For a given cycle an input electron configuration $6s^2 6p^{1-q}$ and charge q are assumed for thallium and the H_{ii} terms are computed. For each of the MO's calculated, a Mulliken population analysis is performed, in which each overlap population is divided equally between the two wave functions involved[25]; the fractional positive output charge on thallium is thus

$$q = 3 - \textstyle\sum_i (c_1^2 + c_1c_2G_{12} + c_1c_3G_{13})_i \,,$$

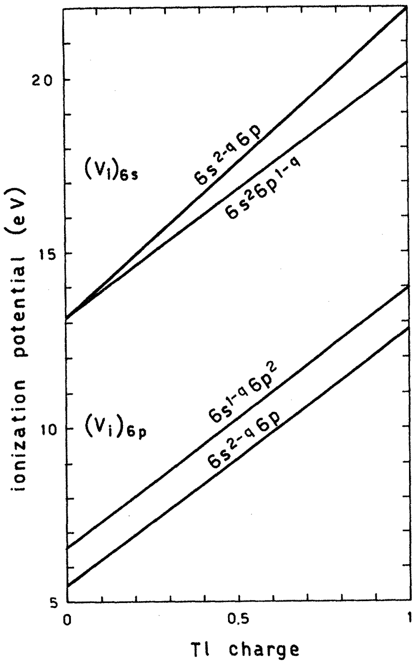

FIG. 2. Ionization potentials of Tl 6s and 6p electrons as a function of charge q and electron configuration.

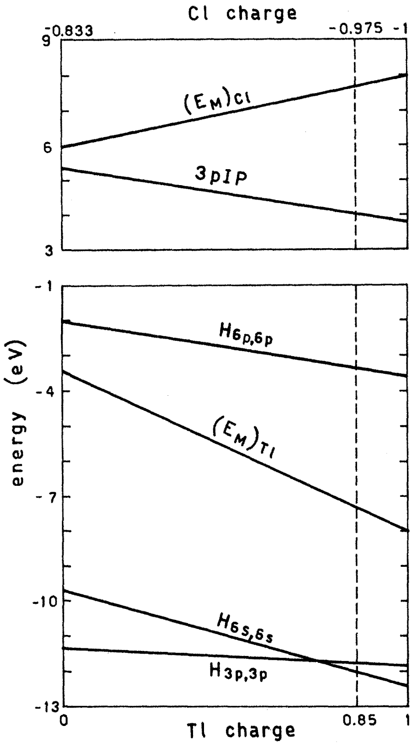

FIG. 3. Ionization potentials of Cl, Madelung energy, and H_{ii} terms as function of Tl and Cl charge.

where the summation is taken over all the a_{1g} and t_{1u} valence electrons. The first term on the right-hand side of the equation represents the charge of the thallium ion without the 6s electrons. The input configuration and charge are altered until a self-consistent result is obtained. The computations were performed with the Tl-Cl distance taken as the ionic radii sum, which turns out to be 6.20 a.u..[18] The final electron population on Tl was $6s^2 6p^{0.15}$ giving an effective charge of 0.85 on Tl and -0.975 on Cl. The corresponding values of H_{ii} terms were $H_{6s,6s} = -12$ eV, $H_{6p,6p} = -3.35$ eV, $H_{3p,3p} = -11.75$ eV (see Fig. 3).

Table I shows the group overlap integrals, the H_{ii} terms used, the λ constants, the computed energy levels, and the corresponding normalized coefficients of the molecular orbitals. Figure 4 shows the molecular-orbital energy diagram. The configuration of the ground state is $(a_{1g}^*)^2$, while that of the first excited state is $(a_{1g}^*)(t_{1u}^*)$. The excitation energy ΔE of the complex is given by the difference $E[(a_{1g}^*)(t_{1u}^*)] - E[(a_{1g}^*)^2]$ and turns out to be 5.3 eV.

The electron population of thallium in the excited state becomes $6s^{1.45}6p^{1.12}$, giving an effective charge of 0.43. Following the above procedure one finds that the corresponding 6s and 6p V_i's are

TABLE I. Group overlap integrals, corrected H_{ii} terms, λ constants, self-consistent MO energies, and normalized coefficients for $(\mathrm{TlCl_6})^{5-}$. The values in parentheses for the coefficients $c_{1,2,3}^*$ are obtained by neglecting the overlap.

MO	G_{ij} for $R=6.20$ a.u.			H_{ii} (eV)				
symmetry	G_{12}	G_{13}	G_{23}	H_{11}	H_{22}	H_{33}	λ_2	λ_3
a_{1g}	0.443	•••	•••	−12.000	−12.925	•••	1.056	•••
t_{1u}	0.406	0.225	0.052	− 3.350	−11.750	−11.985	1.000	1.010
MO		Bonding levels				Antibonding levels		
symmetry	E(eV)	c_1	c_2	c_3	E^*(eV)	c_1^*	c_2^*	c_3^*
a_{1g}	−15.05	0.535	0.640	•••	−5.81	0.979	−0.913	•••
						(0.731)	(−0.682)	•••
t_{1u}	−12.34	0.039	0.575	0.767	−0.49	1.121	−0.492	−0.234
	−11.37	0.037	0.772	−0.665		(0.899)	(−0.395)	(−0.188)

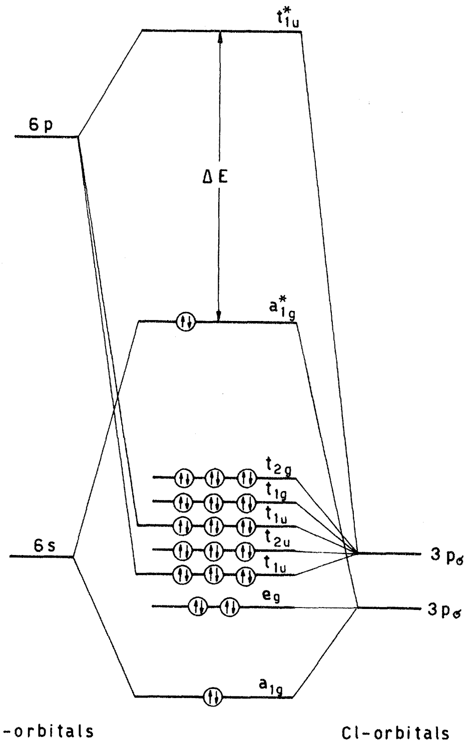

FIG. 4. Molecular-orbital energy-level diagram.

given by

$$(V_i)_{6s}^{q=0.43} = 1.28\,V_i(6s^{1.57}6p) - 0.28\,V_i(6s^2 6p^{0.57})$$
$$= 17.1 \text{ eV},$$

$$(V_i)_{6p}^{q=0.43} = 0.88\,V_i(6s^{1.57}6p) + 0.12\,V_i(6s^{0.57}6p^2)$$
$$= 8.74 \text{ eV}.$$

By adding up E_M for $\mathrm{Tl}^{0.43}$($E_M = -5.4$ eV, see Fig. 3) one obtains for the corresponding H_{ii} terms $H_{6s,6s} = -11.7$ eV, $H_{6p,6p} = -3.34$ eV; the $H_{3p,3p}$ term turns out to be -11.55 eV (see Fig. 3). These values are nearly coincident with the final values in the self-consistent evaluation of the ground-state configuration. Hence, with a good approximation our computation may be considered consistent also for the excited state.

III. COULOMB AND SPIN-ORBIT INTERACTIONS

In order to obtain the energy of the terms ${}^1T_{1u}$, ${}^3T_{2u}$, ${}^3E_u$, ${}^3T_{1u}$, ${}^3A_{1u}$, arising from the $(a_{1g}^*)(t_{1u}^*)$ configuration,[1,26] the exchange and spin-orbit energies must be taken into account. The MO basis functions corresponding to the above terms are reported in Ref. 1; the exchange and spin-orbit interaction matrix results in Table II, where $G = \langle a_{1g}^*(1) t_{1u}^*(2) \mid e^2/r_{12} \mid t_{1u}^*(1) a_{1g}^*(2)\rangle$ is the exchange integral between the a_{1g}^* and t_{1u}^* electrons and ζ is the spin-orbit coupling constant for the t_{1u}^* electron. The exact evaluation of the exchange integral G is tedious since a great number of integrals must be considered; thus an estimation has been carried out by the method of intermediate neglecting of differential overlap (INDO).[27] According to this method, the molecular orbitals are renormalized neglecting the overlap, and only exchange monoatomic integrals and Coulomb integrals are retained. It is easily seen that, neglecting small terms, the exchange integral G becomes

$$G \simeq [c_1(a_{1g}^*)]^2 [c_1(t_{1u}^*)]^2 \langle 6s6p \mid e^2/r_{12} \mid 6p6s\rangle$$
$$+ (6)^{-1} [c_2(a_{1g}^*)]^2 [c_2(t_{1u}^*)]^2 \langle z^2 \mid e^2/r_{12} \mid z^2\rangle = 0.5 \text{ eV},$$

where the coefficients $c_{1,2}$ are given in Table I, the value $\langle 6s6p \mid e^2/r_{12} \mid 6p6s\rangle = 1.008$ eV has been deduced from atomic spectra,[5] and the value $\langle z^2 \mid e^2/r_{12} \mid z^2\rangle = 7.5$ eV was estimated by extrapolation of the values corresponding to the sequence Cl^{4+}, Cl^{3+}, Cl^{2+}, Cl^{+}, Cl^{0}. Each of these values was obtained as a difference between the ionization potential and the electron affinity[28] with data taken from Refs. 19 and 23. Hence, the strong reduction of the exchange energy in going from the free-ion case[5] ($G = 1.008$ eV) to the solid state[2]($G = 0.28$ eV) can be understood in the MO framework.

The term difference also depends on spin-orbit splitting. The effect of covalence on the spin-orbit coupling has been studied by several authors.[29–31] In general, it turns out that spin-orbit coupling effects are smaller for ions in a crystal than for free ions. This effect arises both from a reduction in orbital angular momentum and from a modification of ζ_{ion} in the solid. The orbital reduction factor k which, in our case is given by $k = \langle t_{1u,x}^* \mid \underline{1} \mid t_{1u,y}^*\rangle / \langle 6p_x \mid \underline{1} \mid 6p_y\rangle$ has been evaluated by the method outlined in Ref. 31 and turns out to be

$$k = c_1^2 + \sqrt{8}\,c_1 c_2 S_\sigma + 4 c_1 c_3 S_\pi + \tfrac{1}{2} c_3^2 - \sqrt{2}\,c_2 c_3 = 0.56,$$

where c_1, c_2, c_3 are the coefficients for the t_{1u}^* antibonding oribital (Table I) and $S_\sigma = \langle 6p_x \mid z_1\rangle = 0.287$ and $S_\pi = \langle 6p_x \mid y_2\rangle = 0.114$. To find the effective spin-orbit coupling we must calculate the matrix elements of $\zeta\underline{1}$. This is completely analogous to the calculation of the effective orbital angular momentum, and one obtains

$$\zeta_{\mathrm{eff}} = c_1^2 \zeta_{\mathrm{Tl}} + \sqrt{8}\,c_1 c_2 \zeta_{\mathrm{Tl}}^{\sigma} S_\sigma + 4 c_1 c_3 \zeta_{\mathrm{Tl}}^{\pi} S_\pi + \tfrac{1}{2} c_3^2 \zeta_{\mathrm{Cl}}$$

TABLE II. Exchange and spin-orbit interaction matrix.

	${}^1T_{1u}$	${}^3T_{2u}$, ${}^3E_u$	${}^3T_{1u}$	${}^3A_{1u}$
${}^1T_{1u}$	G	0	$(1/\sqrt{2})\zeta$	0
${}^3T_{2u}$, ${}^3E_u$	0	$-G+\frac{1}{2}\zeta$	0	0
${}^3T_{1u}$	$(1/\sqrt{2})\zeta$	0	$-G-\frac{1}{2}\zeta$	0
${}^3A_{1u}$	0	0	0	$-G-\zeta$

$$-\sqrt{2}\,c_2 c_3 \zeta_{\mathrm{Cl}}\,, \quad (3)$$

where ζ_{Tl} and ζ_{Cl} are the spin-orbit constants for the central atom and the ligands corrected by taking into account their effective charges, and $\zeta_{\mathrm{Tl}}^{\sigma,\pi}$ are the spin-orbit constants in the overlap regions.

As in the excited state, the electron population on Tl is found to be $\sim 6s^{1.5}6p^1$, the value of $\zeta_{\mathrm{Tl}} = 6689\ \mathrm{cm}^{-1}$ was obtained by interpolating the values[19] $\zeta_{\mathrm{Tl}^0} = 5195\ \mathrm{cm}^{-1}$ and $\zeta_{\mathrm{Tl}^+} = 8183\ \mathrm{cm}^{-1}$ corresponding to the configuration $6s^26p$ and $6s6p$ of Tl^0 and Tl^+, respectively.

The value of ζ_{Cl} for the chlorine ion was obtained by extrapolation of the sequence Cl^{3+}, Cl^{2+}, Cl^{+}, Cl^{0} with data obtained by Moore.[19] We obtain in this fashion $\zeta_{\mathrm{Cl}} \simeq 400\ \mathrm{cm}^{-1}$, hence, the contributions from ligands can be neglected.

An estimation of $\zeta_{\mathrm{Tl}}^{\sigma,\pi}$ was carried out by assuming that ζ varies roughly as $1/r^3$, thus we have

$$\zeta_{\mathrm{Tl}}^{\sigma,\pi} = \zeta_{\mathrm{Tl}} \frac{\langle r^{-3}\rangle_{\sigma,\pi}}{\langle r^{-3}\rangle_{\mathrm{Tl}}} = \zeta_{\mathrm{Tl}} \frac{\langle 3p_{\sigma,\pi} \mid r^{-3} \mid 6p_{\sigma,\pi}\rangle}{\langle 3p_{\sigma,\pi} \mid 6p_{\sigma,\pi}\rangle} \frac{1}{\langle 6p \mid r^{-3} \mid 6p\rangle} \,.$$

Substituting numerical values we find $\zeta_{\mathrm{Tl}}^{\sigma} = 3665\ \mathrm{cm}^{-1}$ and $\zeta_{\mathrm{Tl}}^{\pi} = 2368\ \mathrm{cm}^{-1}$. Substituting in (3) we obtain $\zeta_{\mathrm{eff}} = 0.8$ eV which is in good agreement with the experimental value of $\zeta_{\mathrm{eff}} = 0.69$ eV, observed in KCl : Tl.[2] Another estimation of ζ_{eff} has been carried out by neglecting the contributions from the overlap regions and using, accordingly, molecular orbitals normalized neglecting the overlap. We obtain, in this fashion, $\zeta_{\mathrm{eff}} = c_1^2 \zeta_{\mathrm{Tl}} \simeq 0.7$ eV. Thus, the two different evaluations of ζ_{eff} are in good agreement and confirm the reduction of spin-orbit coupling effects in the solids.

IV. COMPARISON OF THEORETICAL RESULTS WITH EXPERIMENTS

In Table III a comparison is shown between the theoretical values for the parameters W_0,[32] G, ζ and the values determined from observed A-, B-, and C-band positions.[2] The values corresponding to the free Tl^+ ion[5] are also reported. It is seen that the molecular-orbital calculation provides an explanation of the reduction of the quantities W_0, G, ζ in going from the free-ion case to the solid state.

TABLE III. Comparison between the values of parameters W_0, G, and ζ experimentally derived and the theoretical ones.

Parameter (eV)	Experimentally derived free	KCl : Tl	MO computation
W_0	8.180	5.875	5.9
G	1.008	0.28	0.5
ζ	1.015	0.69	0.8

TABLE IV. Comparison between the experimental absorption energies and the theoretical ones.

Band	Transition	Expt band max (eV)	MO computation (eV)
A	${}^1A_{1g} \rightarrow {}^3T_{1u}$	5.03	4.8
B	${}^1A_{1g} \rightarrow {}^3T_{2u}, {}^3E_u$	5.94	5.8
C	${}^1A_{1g} \rightarrow {}^1T_{1u}$	6.36	6.6

The energy levels, relative to the ${}^1A_{1g}$ ground state, are then evaluated by the formulas[8]

$$W({}^3A_{1u}) = W_0 - G - \zeta\,,$$

$$W({}^3T_{1u}) = W_0 - \tfrac{1}{4}\zeta - \left[(G + \tfrac{1}{4}\zeta)^2 + \tfrac{1}{2}\zeta^2\right]^{1/2},$$

$$W({}^3E_u, {}^3T_{2u}) = W_0 - G + \tfrac{1}{2}\zeta$$

$$W({}^1T_{1u}) = W_0 - \tfrac{1}{4}\zeta + \left[(G + \tfrac{1}{4}\zeta)^2 + \tfrac{1}{2}\zeta^2\right]^{1/2}.$$

Table IV shows a comparison between the experimental values of the A, B, and C absorption band maxima[2] and the theoretical ones; as can be seen, the agreement is quite satisfactory.

In our theoretical treatment of KCl : Tl, we have considered only the absorption bands and hence, as a first approximation we have neglected the Jahn-Teller effect (JTE) which according to some authors,[33] is responsible for the fine structure of the A and C bands. However, serious objections have been raised by the use of the adiabatic approximation and when this approximation is not employed one finds no splitting of the absorption bands.[34–36]

In dealing with emission spectrum the JTE plays an important role and can be no longer neglected.[1]

V. CONCLUSION

It has been shown that a semiempirical MO calculation provides a consistent interpretation of the A, B, C absorption bands of KCl : Tl. The results here obtained suggest that the covalent bonding effects are of great importance in understanding the properties of luminescence centers in alkali halide phosphors activated by heavy metals.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor G. Toraldo di Francia and Professor D. L. Dexter for helpful discussions and suggestions. Thanks are also due to R. Mazzini, who wrote the computer program.

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[32] W_0 is the one-electron energy difference ΔE between the configurations $(a_{1g}^*)(t_{1u}^*)$ and $(a_{1g}^*)^2$ corrected by the difference $\Delta J = \langle a_{1g}^*(1)\, t_{1u}^*(2) \,|e^2/r_{12}|\, a_{1g}^*(1) t_{1u}^*(2)\rangle - \langle a_{1g}^*(1) a_{1g}^*(2) \,|e^2/r_{12}|\, a_{1g}^*(1) a_{1g}^*(2)\rangle$ between the Coulomb energy corrections to the configurations $(a_{1g}^*)(t_{1u}^*)$ and $(a_{1g}^*)^2$, respectively. The quantity ΔJ has been estimated in the INDO approximation and it is seen that neglecting small terms, ΔJ becomes $\Delta J \simeq [c_1(a_{1g}^*)]^2 [c_1(t_{1u}^*)]^2 \times \langle 6s6p|e^2/r_{12}|6s6p\rangle - [c_1(a_{1g}^*)]^4 \langle 6s^2|e^2/r_{12}|6s^2\rangle - (6)^{-1} \times \{[c_2(a_{1g}^*)]^4 - [c_2(a_{1g}^*)]^2 [c_2(t_{1u}^*)]^2\} \langle z^2|e^2/r_{12}|z^2\rangle = 0.6$ eV, where the coefficients $c_{1,2}$ are given in Table I, the value $\langle z^2 | e^2/r_{12} | z^2\rangle = 7.5$ eV above reported has been used, and the values $\langle 6s^2 | e^2/r_{12} | 6s^2\rangle = 8.19$ eV and $\langle 6s6p | e^2/r_{12} | 6s6p\rangle = 7.20$ eV have been computed starting from functions (2). Thus, one has $W_0 = \Delta E + \Delta J = 5.9$ eV.

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PHYSICAL REVIEW B VOLUME 3, NUMBER 11 1 JUNE 1971

Coupling Coefficients for the Indirect Nuclear Dipole Interaction in Indium by Nuclear Quadrupole Resonance

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(Received 8 February 1971)

Moment analysis of the NQR spectrum of indium metal is used to measure its isotropic and anisotropic dipolar interactions. The coupling coefficients $\tilde{A}$ and $\tilde{B}$ are measured to be 2.46×10^{-46} and 1.55×10^{-46} erg cm^3, respectively. The measurement of the NQR in In-Sn alloys is described and found to be in qualitative agreement with earlier NMR results.

I. INTRODUCTION

The dipolar interaction between conduction electrons and atomic nuclei provides valuable means for experimental verification of theories concerning conduction electrons. Knight shifts have been the subject of much investigation in this regard.[1] Evaluation of the Knight-shift parameters from the observed data is most easily achieved for systems with cubic crystal structure, or with nuclear spin