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R center in KCl. I. Point-ion electronic-structure calculation with application to magneto-optical parameters*

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The electronic structure of the *R* center in KCl is investigated theoretically by means of a molecular-orbital calculation with configuration mixing. The molecular orbitals, represented by single-center expansions in Slater-type orbitals, are used to construct an extensive set of configurations. A point-ion potential is assumed in the calculation. The resulting energy levels are correlated with the excited states associated with observed optical-absorption bands and give further confirmation of the symmetry assignments for the bands which were previously made on the basis of experiment. The corresponding wave functions are employed in a calculation of the spin-orbit constant and orbital *g* value (magneto-optical parameters) associated with the ground electronic state, where the molecular orbitals are orthogonalized to surrounding ion-core orbitals. The calculated magneto-optical parameters are in good agreement with experiment.

I. INTRODUCTION

The Van Doorn[1] model for the *R* center, shown in Fig. 1, consists of an aggregate of three adjacent *F* centers which form an equilateral triangle in the (111) plane. The *R* center gives rise to a series of optical-absorption bands, some of which are obscured by much stronger absorptions associated with *F* and *M* centers. The R_1 and R_2 bands were first observed by Molnar.[2] The R_F band was identified by Okamoto[3] in polarized bleaching experiments. Silsbee[4] used stress-induced dichroism to isolate the four bands labeled R_N, R_M, R_B, and R_K. Silsbee also investigated the effect of stress splitting of the R_2-band zero-phonon line, showing that the ground electronic state is an orbitally degenerate spin doublet. The lowest quartet states have been investigated by Seidel, *et al.*[5] and by Ortega.[6] As a result of these experiments, the energies and the corresponding symmetries, which characterize the electronic structure of the *R* center in KCl, are well known.

Duval, Gareyte, and Merle-D'Aubigne[7] have observed magnetic circular dichroism (MCD) associated with the *R* center in KCl. Subsequent MCD measurements have been reported.[8-11] The reduced spin-orbit constant and reduced orbital *g* value were inferred by noting the dependence of the dichroism on temperature and applied magnetic field. (By "reduced" we mean that the purely electronic values are reduced by the effects of lattice motion.) The unreduced spin-orbit constant and unreduced orbital *g* value have been measured by Krupka and Silsbee[12] by observing the stress dependence of the *g* shift. The electron-spin-resonance signal observed in this experiment is associated with the ground electronic state of the *R* center in KCl.

The present article is concerned with an electronic-structure calculation of the *R* center in KCl in the rigid-lattice point-ion approximation. Energies of low-lying excited states are calculated, and the ground-state wave function is used to determine the spin-orbit coupling constant and orbital *g* value. *A priori* calculations of the electron-lattice interaction, simulation of the R_2-band absorption line shape, and evaluation of the Jahn-Teller coupling constant are reported in the following.

The electronic-structure calculations of the *R* center may be divided into two categories: those which employ a continuum potential and those which employ a point-ion potential.[13] Silsbee[4] has adapted Hirschfelder's[14] calculation of the H_3 molecule to the *R* center in KCl. Wang and Chu[15] have performed *R*-center calculations using intermediate polaron coupling. Both of these models employ a continuous representation of the lattice. More recent electronic-structure calculations[16-19] have employed a point-ion potential, which retains the translational and rotational features of the true lattice potential. These point-ion calculations share one feature in common: They all employ Heitler-London wave functions. In the calculations of Maisonneuve and Margerie,[19] configuration

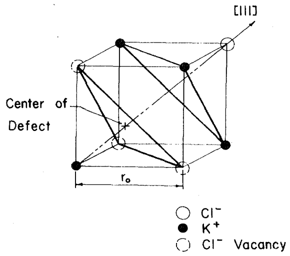

FIG. 1. Geometry of the *R* center in KCl. Three electrons are trapped at the triangle of anion vacancies.

mixing is included to correct for the exaggerated correlation effects which occur when Heitler-London wave functions are used.

The present electronic-structure calculation is based on self-consistent-field molecular-orbital theory with extensive configuration mixing. The trial configurations are constructed from single-particle orbitals consisting of *s*, *p*, and *d* Slater-type orbitals (STO's), expanded about the geometrical center of the defect. The linear coefficients and exponential parameters are varied in order to minimize the energy corresponding to the dominant configuration of each symmetry type. The configuration mixing yields a ground electronic state and low-lying excited states from which transition energies are calculated and compared with the observed optical-absorption bands.

The first theoretical treatment of the spin-orbit coupling constant and the orbital *g* value (magneto-optical parameters) was the semiempirical calculation of Krupka and Silsbee[12] for the ground state of the *R* center in KCl. This calculation was extended by Margerie and Martin-Brunetiere,[20] where a different set of polar configurations was considered. An *ab initio* calculation due to Maisonneuve and Margerie[19] employs the wave functions developed therein, orthogonalized to surrounding ion-core orbitals.

In the present investigation, the magneto-optical parameters are calculated for the ground state of the *R* center in KCl by the same procedure, but using wave functions generated by a molecular-orbital approach. Since there are no adjustable parameters in this model, the present treatment also represents an *ab initio* calculation.

In Sec. II, we describe the theory of the electronic-structure calculations which have been utilized in the present work. Section III contains the theory of the magneto-optical parameters. The results of the present calculation are presented in Sec. IV, with a discussion following in Sec. V.

II. THEORY OF THE ELECTRONIC-STRUCTURE CALCULATIONS

The electronic-structure calculations in the present work are based on an open-shell molecular-orbital method[21,22] with configuration mixing. The point-ion model[13] for the crystal field is also incorporated, with the point-ion potential expanded about the defect center. In the point-ion model, the ions which constitute the crystal are represented as point charges located at the rigid-lattice sites. Gourary and Fein[23] have shown that the point-ion potential is a model pseudopotential, thus justifying the neglect of extended-ion effects in calculating the electronic structure.

The molecular orbitals associated with the excess electrons are expanded in terms of STO's about the center of the defect. These single-center expansions allow for the development of closed-form expressions for the matrix elements of the Hamiltonian. In the *R* center, the anion vacancies do not contain strong centers of force for the excess electrons; consequently, the single-center expansion is more appropriate in this case than a molecular orbital constructed from a linear combination of vacancy-centered functions and is far more expedient. Configuration mixing is included both to incorporate correlation effects and to provide a valid representation of excited states. Since the *R* center contains three excess electrons, all configurations are open shell; i.e., there is at least one molecular orbital which is only partially populated.

A. One-electron orbital and potential expansions

The geometry of the *R* center is shown in Fig. 1 with the ions at their rigid-lattice positions. The point group of the *R* center is C_{3v} with the triad axis along [111]. The origin of coordinates is taken at the center of the defect (i.e., the center of the equilateral triangle of vacancies). The polar angle θ is measured with respect to the [111] axis, while the azimuthal angle ϕ is measured in the plane of the vacancies.

The one-electron orbitals are expanded in terms of the basis functions $\chi_{p\lambda\sigma}$, which are taken to be linear combinations of STO's. The STO's are of the form

$$\psi_{t\lambda\sigma}(\vec{r}) = [(2\zeta_t)^{2n_t+1}/(2n_t)!]^{1/2} r^{n_t-1} e^{-\zeta_t r} \mathcal{Y}_t^{\lambda\sigma}(\theta,\phi), \tag{1}$$

where ζ_t is an exponential variational parameter which is ultimately adjusted to minimize the electronic energy, n_t is an integer, and $\mathcal{Y}_t^{\lambda\sigma}$ is a linear combination of spherical harmonics which transforms like the σth row of the λth irreducible representation of the point group of the defect. For deriving the closed-form expressions for the matrix elements of the two-electron operators in the Hamiltonian, the assumption that $n_t > l_t$ is useful, where l_t is the order of the spherical harmonics contained in $\mathcal{Y}_t^{\lambda\sigma}$. This restriction on n_t is retained throughout. The pth basis function is given by

$$\chi_{p\lambda\sigma} = \sum_t a_{pt\lambda}\, \psi_{t\lambda\sigma}, \tag{2}$$

where the linear coefficients $a_{pt\lambda}$ are specified.

The ith one-electron orbital expanded in terms of the basis functions is given by

$$\phi_{i\lambda\sigma}=\sum_{p}\chi_{p\lambda\sigma}C_{\lambda p i}=\chi^{\dagger}_{\lambda\sigma}C_{\lambda i}\,, \tag{3}$$

where the expansion coefficients $C_{\lambda p i}$ are independent of the row of the irreducible representation and $\chi_{\lambda\sigma}$ and $C_{\lambda i}$ are vectors.

The point-ion potential of the lattice is expanded in spherical harmonics,

$$V_{\mathrm{PI}}(\vec{\mathrm{r}})=-\sum_{L=0}^{\infty}\sum_{M=-L}^{L}Y_L^M(\theta,\phi)\Big(e_{LM}r^L+\sum_{\alpha<}f_{LM\alpha}(r_\alpha^L r^{-L-1}-r^L r_\alpha^{-L-1})\Big), \tag{4}$$

where

$$e_{LM}=\sum_{\alpha=0}^{\infty}\frac{8\pi Q_\alpha}{(2L+1)r_\alpha^{L+1}}Y_L^{M*}(\theta_\alpha,\phi_\alpha) \tag{5}$$

and

$$f_{LM\alpha}=\frac{8\pi Q_\alpha}{2L+1}Y_L^{M*}(\theta_\alpha,\phi_\alpha)\,. \tag{6}$$

In these expressions, $(r_\alpha,\theta_\alpha,\phi_\alpha)$ denotes the position of the αth ion, which has a charge Q_α. Y_L^M is a spherical harmonic, and $\sum_{\alpha<}$ denotes that the summation is restricted to all ions for which $r_\alpha < r$. The infinite sum required for the evaluation of e_{LM} is performed by the method of Nijboer and DeWette.[24] The terms in the summations over L and M, in practice, are limited by symmetry considerations to a finite number, since the number of basis functions for the one-electron orbitals is restricted to make the computations tractable. Slater atomic units are used throughout; i.e., distances are in Bohr radii and energies in rydbergs.

B. Open-shell molecular-orbital theory

Roothaan has developed a method for performing open-shell molecular-orbital (MO) calculations.[21,22] This method is applicable only to cases in which the energy of the open-shell MO can be written in a particular form. This section relies heavily on Roothaan's work, and the reader is referred to Refs. 21 and 22.

Roothaan's method is applicable to any configuration for which the energy is expressible as[21]

$$\begin{aligned}E=2\sum_k H_k+\sum_{kl}(2J_{kl}-K_{kl})&\\+f\Big(2\sum_m H_m+f\sum_{mn}(2aJ_{mn}-bK_{mn})&\\+2\sum_{km}(2J_{km}-K_{km})\Big)&\,,\end{aligned} \tag{7}$$

where subscripts k and l refer to closed shells, and subscripts m and n to open shells. The first two sums in Eq. (7) represent the closed-shell energy; the second two sums, the open-shell energy; the last sum, the interaction of open and closed shells. The number f is the fractional occupancy of the open shell, and the numerical constants a and b depend on the specific case. The quantities H_i, J_{ij}, and K_{ij} are, respectively, matrix elements of the one-electron, Coulomb, and exchange operators.

Application of the variational principle to Eq. (7) with an orthogonality constraint, and subsequent elimination of off-diagonal Lagrange multipliers, yields distinct self-consistent field (SCF) equations for closed and open shells.[21] When the molecular orbitals are expanded in terms of symmetry-adapted basis functions as in Eq. (3), these SCF equations have the form

$$F_{c\lambda}C_{\lambda k}=\epsilon_{\lambda k}S_\lambda C_{\lambda k} \tag{8}$$

and

$$F_{o\lambda}C_{\lambda m}=\epsilon_{\lambda m}S_\lambda C_{\lambda m} \tag{9}$$

for closed and open shells, respectively, where S_λ is the overlap matrix for basis functions of λ symmetry. The Fock operators $F_{c\lambda}$ and $F_{o\lambda}$, defined in Ref. 22, are functions of all the C's. Thus the SCF equations are implicitly coupled, and must be solved simultaneously by an iterative procedure.

C. Configuration mixing

In order to include electron correlation effects, and to provide a representation of excited states, the configurations formed by populating the various molecular orbitals are allowed to interact. Each eigenstate of the many-electron system is then represented by a superposition of configurations.

The lth state wave function with a particular symmetry and multiplicity can be written as

$$\Psi_l^{\lambda\sigma\zeta}=\sum_j d_{lj}\Phi_j^{\lambda\sigma\zeta}\,, \tag{10}$$

where the configurational terms $\Phi_j^{\lambda\sigma\zeta}$ are linear combinations of Slater determinants of the form

$$\Phi_j^{\lambda\sigma\zeta}=\sum_k D_{jk}\mathcal{A}\prod_i[\phi_i(i)\eta(i)]_k\,. \tag{11}$$

Here, $\Phi_j^{\lambda\sigma\zeta}$ transforms like the σth row of the λth irreducible representation with spin multiplicity ζ, and the coefficients D_{jk} are determined by symmetry. The $\eta(i)$ are the one-electron spin functions, and $\mathcal{A}$ is the antisymmetrizer.

The expansion coefficients d_{lj} are determined by diagonalizing the total system Hamiltonian which leads to the following eigenvalue equation:

$$\sum_n H^{\lambda\sigma\xi}_{mn} d_{ln} = E^{\lambda\xi}_l d_{ln} , \tag{12}$$

where

$$H^{\lambda\sigma\xi}_{mn} = (\Phi^{\lambda\sigma\xi}_m , \; H\Phi^{\lambda\sigma\xi}_n) . \tag{13}$$

The solution of Eq. (13) yields approximate wave functions and upper bounds on the energy levels for each symmetry and multiplicity. Only the few lowest eigenvalues of H_{mn} provide close approximations to the energies of excited states, so many more configurations are required than the number of states of interest.

III. SPIN-ORBIT CONSTANT AND ORBITAL g VALUE

The spin-orbit constant and the orbital g value appear in expressions which describe the stress dependence of the parallel g shift[12] and the temperature and magnetic field dependence of the magnetic circular dichroism.[8,9] In unreduced (electronic) form, the spin-orbit constant and orbital g value appropriate to the R-center ground state are defined respectively as[12]

$$\lambda_E \equiv -2i \left\langle \Psi(^2E_y) \middle| \sum_{\alpha i} \xi_{\alpha c} \vec{\mathrm{l}}_{\alpha, i} \cdot \vec{\mathrm{s}}_i \middle| \Psi(^2E_x) \right\rangle \tag{14}$$

and

$$g_{oE} \equiv -i \left\langle \Psi(^2E_x) \middle| \sum_i l^z_{0,i} \middle| \Psi(^2E_x) \right\rangle . \tag{15}$$

The ionic spin-orbit operator is denoted $\zeta_{\alpha c}(r)$, where

$$\xi_{\alpha c}(r) = \left(\frac{\alpha_F^2}{2r} \right) \left(\frac{\partial V_{\alpha c}(r)}{\partial r} \right) . \tag{16}$$

$V_{\alpha c}(r)$ is the Hartree potential associated with core state c of ion α, and α_F is the fine-structure constant. The orbital angular momentum operator for the ith electron taken about the αth surrounding ion is denoted $\vec{\mathrm{l}}_{\alpha, i}$ and the corresponding spin operator is $\vec{\mathrm{s}}_i$. The symbol $\vec{\mathrm{l}}_{0, i}$ represents the orbital angular momentum taken about the geometrical center of the defect.

In the present formulation, the ground electronic state is approximated by the single and dominant configuration of lowest energy; hence

$$\Psi(^2E_x) = \left| 1a_1^2 1e_x \right\rangle \tag{17}$$

and

$$\Psi(^2E_y) = \left| 1a_1^2 1e_y \right\rangle . \tag{18}$$

The results of the electronic-structure calculation, described in the following section, support this identification. In terms of the molecular orbitals for the R center, λ_E and g_{0E} are given by

$$\lambda_E = -i \left\langle 1e_y \middle| \sum_\alpha \xi_{\alpha c} l^z_\alpha \middle| 1e_x \right\rangle \tag{19}$$

and

$$g_{oE} = -i \langle 1e_y | l^z_0 | 1e_x \rangle . \tag{20}$$

Smith[25] has shown that it is necessary to orthogonalize these molecular orbitals to the surrounding ion-core orbitals. Assuming that the normalization factor is negligible, the orthogonalized orbitals, $|e_i\rangle$, may be written in terms of the pseudo-orbitals, $|i\rangle$, as

$$|e_i\rangle = |i\rangle - \sum_{\alpha c} \Omega_{i\alpha c} |\alpha c\rangle , \tag{21}$$

where i takes the values x, y. The ket, $|\alpha c\rangle$, denotes core state c on ion α, and the $\Omega_{i\alpha c}$ are overlap integrals defined by

$$\Omega_{i\alpha c} \equiv \langle \alpha c | i \rangle . \tag{22}$$

A. Spin-orbit constant

The spin-orbit constant is expanded in terms of pseudo-orbitals and ion-core orbitals as

$$\begin{aligned} \lambda_E = -i \sum_\alpha \Bigg(& \langle y | \xi_{\alpha c} l^z_\alpha | x \rangle - \sum_{\alpha' c'} (\langle \alpha' c' | \xi_{\alpha c} l^z_\alpha | x \rangle \Omega^*_{y\alpha' c'} + \langle y | \xi_{\alpha c} l^z_\alpha | \alpha' c' \rangle \Omega_{x\alpha' c'}) \\ & + \sum_{\alpha' c'} \sum_{\alpha'' c''} \langle \alpha' c' | \xi_{\alpha c} l^z_\alpha | \alpha'' c'' \rangle \Omega^*_{y\alpha' c'} \Omega_{x\alpha'' c''} \Bigg) . \end{aligned} \tag{23}$$

Smith has shown that the first three terms constitute less than 10% of the total result for the F center. These terms are neglected in the present treatment. In addition, it is assumed that the matrix elements which connect core states on different ions are vanishingly small; hence

$$\lambda_E \simeq -i \sum_\alpha \sum_{cc'} \Omega^*_{y\alpha c} \Omega_{x\alpha c'} m_c \zeta_{\alpha cc'} , \tag{24}$$

where

$$\zeta_{\alpha cc'} \equiv \langle \alpha c | \xi_{\alpha c} | \alpha c' \rangle . \tag{25}$$

The ionic spin-orbit coupling constant $\zeta_{\alpha cc'}$ is evaluated for the $2p$ and $3p$ states of K^+ and Cl^- using the radial wave function of Clementi.[26] The average value of $\xi_{\alpha 2p}$ and $\xi_{\alpha 3p}$ is used for the off-diagonal elements $\zeta_{\alpha 2p3p}$.

B. Orbital *g* value

The orbital g value is expanded in pseudo-orbitals and ion-core orbitals as in Eq. (24). In the last term, it is necessary to translate the origin about which l_0^z operates[12]; hence

$$l_0^z = l_\alpha^z + (\vec{d}_{0\alpha} \times \vec{p})^z , \tag{26}$$

where $d_{0\alpha}$ is a vector connecting the center of the defect with ion α, and $\vec{p}$ is the linear momentum operator. The dipole approximation is employed, so that, in Slater atomic units,

$$\vec{p} = -i[\vec{r}, H_0]/2 . \tag{27}$$

H_0 is the Hamiltonian for the isolated ion, where

$$H_0 |\alpha c\rangle = E^0_{\alpha c} |\alpha c\rangle . \tag{28}$$

The orbital g value then assumes the form

$$g_{oE} = -i\langle y | l_0^z | x\rangle + i \sum_{\alpha c} (\langle y | l_0^z | \alpha c\rangle \Omega_{x\alpha c} + \langle \alpha c | l_0^z | x\rangle \Omega^*_{y\alpha c} - \Omega^*_{y\alpha c} \Omega_{x\alpha c} m_c)$$
$$+ \tfrac{1}{2} \sum_{\alpha c c'} \Omega^*_{y\alpha c'} \Omega_{x\alpha c} (E^0_{\alpha c'} - E^0_{\alpha c})(d^x_{0\alpha} Y_{\alpha c' c} - d^y_{0\alpha} X_{\alpha c' c}) , \tag{29}$$

where m_c is the azimuthal quantum number of core orbital $|\alpha c\rangle$, and where $X_{\alpha c' c}$ and $Y_{\alpha c' c}$ are defined by

$$X_{\alpha c' c} \equiv \langle \alpha c' | x | \alpha c\rangle , \tag{30}$$

and

$$Y_{\alpha c' c} \equiv \langle \alpha c' | y | \alpha c\rangle . \tag{31}$$

IV. COMPUTATIONAL RESULTS

The theory presented in the previous sections has been applied to the R center in KCl. The results of these calculations are presented here.

A. One-electron calculations

Before embarking on the elaborate electronic-structure calculations of the R center using molecular-orbital theory and configuration mixing, the one-electron energy levels were computed for the R^{2+} center. These calculations were performed in order to obtain preliminary insight into the nature of the orbitals, which were subsequently used to construct the configurations.

The one-electron orbitals are expanded in terms of the basis functions as given by Eq. (3). The expansion coefficients are determined from a variational principle, which minimizes the electronic energy. For the one-electron orbital problem in the point-ion model considered here, the Hamiltonian consists only of the one-electron operators f_i, which are given by

$$f_i = -\nabla_i^2 + V_{\mathrm{PI}}(\vec{r}) , \tag{32}$$

where $V_{\mathrm{PI}}(\vec{r})$ is given by Eq. (4).

The variational problem reduces to diagonalizing this Hamiltonian, which is equivalent to solving the eigenvalue equations

$$F_\lambda C_{\lambda k} = \epsilon_{\lambda k} S_\lambda C_{\lambda k} , \tag{33}$$

where F_λ and S_λ are the one-electron Hamiltonian and the overlap matrices, respectively, in that portion of the space defined by the ϕ basis set [see Eq. (3)] which transforms like the λth irreducible representation. Equation (33) reflects the fact that F and S can be partitioned by symmetry considerations. $\epsilon_{\lambda k}$ is the kth one-electron energy level corresonding to the λth irreducible representation. It should be noted that F depends on the variational parameters ζ_t defined in Eq. (1). Thus it is necessary to solve Eq. (33) for various values of ζ_t. The optimum value of ζ_t corresponds to the minimum of the lowest one-electron energy level.

For the s-type basis function, the two lowest-order STO's are used in order to preserve the normalization and the continuity of the wave function at the origin. The explicit forms of the radial components of the basis functions are

$$R_1(r) = (4\zeta^3/7)^{1/2}(1+\zeta r)e^{-\zeta r}, \quad l = 1 \tag{34}$$

and

$$R_l(r) = [(2\zeta)^{2l+1}/(2l)!]^{1/2} r^{l-1} e^{-\zeta r}, \quad l > 1 . \tag{35}$$

Table I summarizes the basis-function set for the molecular orbitals used in the R-center electronic calculations. It should be noted that with this ba-

TABLE I. Basis-function set for R-center molecular orbitals.

A_1	$E(1)$	$E(2)$
$R_0Y_0^0$ (s)	$R_1Y_1^{-1}$ (p)	$-R_1Y_1^1$ (p)
$R_1Y_1^0$ (p)	$R_2Y_2^2$ (d_1)	$R_2Y_2^{-2}$ (d_1)
$R_2Y_2^0$ (d)	$R_2Y_2^{-1}$ (d_2)	$-R_2Y_2^1$ (d_2)

TABLE II. Optimum variational parameters for one-electron orbitals for R^{2+} center in KCl. The variational parameters are in units of inverse Bohr radii.

Basis function	ζ
A_1 orbitals	
s	0.61
p	0.65
d	0.95
E orbitals	
p	0.46
d_1	0.68
d_2	0.57

sis set only A_1- and E-symmetry one-electron orbitals can be formed. The two E-symmetry basis functions which contain the R_2 radial functions are allowed to have different variational parameters.

With the above basis-function set, only terms up to and including $L=4$ survive in matrix elements of the point-ion potential. In addition, the present calculations are based on considering the first 51 shells of ions in the direct lattice summations required for the potential computations. The incorporation of f orbitals would allow an azimuthal variation in A_1 symmetry as well as providing one-electron orbitals of A_2 symmetry, but would greatly increase the complexity of the calculation.

The optimum parameter sets for the A_1 and E molecular orbitals are given in Table II. The corresponding one-electron energy levels and linear coefficients are listed in Table III. These results show that the lowest one-electron orbital has A_1 symmetry.

B. Open-shell molecular-orbital calculations

The nine molecular orbitals described in the preceding section can be used to generate 53 distinct configurations for the three-electron R center, consistent with the Pauli exclusion principle. Each configuration is formed by populating the molecular orbitals. In order to obtain an initial estimate of the ordering of these configurations according to energy, the sum of the one-electron energies for the populated MO's, as obtained in the preceding section, was used. The results are shown in Table IV for the ten lowest configurations. Table IV suggests that the ground state is a doublet E state.

Each configuration is constructed by populating three molecular spin orbitals. These configurations can be decomposed into individual terms which transform like a particular row of one of the irreducible representations of C_{3v}. Since there are three electrons, the spin multiplicity of each term is either doublet or quartet. Table IV shows the terms which correspond to each of the ten lowest configurations.

An MO calculation is carried out for the lowest-energy configurational term for each of the three irreducible representations of C_{3v}: A_1, A_2, and E. The ionic conformation for these calculations is the rigid lattice. The results of the MO calculations yield all the molecular orbitals which are used to construct the configurational terms of the corresponding symmetry. These calculations are performed only for either a doublet or a quartet state of each symmetry for which the criterion of Eq. (7) could be satisfied. In order to select the appropriate lowest terms of each symmetry, the sums of the one-electron energies as given in

TABLE III. One-electron energy levels and linear coefficients for R^{2+} center in KCl. The energies are in units of rydbergs.

A_1 orbitals					
k	Orbital designation	ϵ_k	C_{sk}	C_{pk}	C_{dk}
1	$1a_1$	−1.1015	0.8955	−0.4033	0.1882
2	$2a_1$	−0.8425	0.4438	0.8414	−0.3085
3	$3a_1$	−0.3061	−0.0339	0.3597	0.9324
E orbitals					
k	Orbital designation	ϵ_k	C_{pk}	C_{d_1k}	C_{d_2k}
1	$1e$	−0.8544	0.9753	−0.0978	0.1983
2	$2e$	−0.6882	−0.2187	−0.5601	0.7991
3	$3e$	−0.5919	−0.0329	0.8227	0.5676

TABLE IV. Ten lowest configurations for *R* center in KCl estimated from the calculated single-particle energies of the R^{2+} center. The energies are in units of rydbergs. Relative energies are also listed in electron volts, in order to facilitate comparison with Table VIII.

Configuration	Terms	Estimated energy (Ry)	Relative energy (eV)
$1a_1^2 1e$	^2E	−3.0574	0.00
$1a_1^2 2a_1$	$^2A_1$	−3.0455	0.16
$1a_1^2 2e$	^2E	−2.8912	2.26
$1a_1 1e^2$	$^2A_1+{}^2A_2+{}^2E+{}^4A_2$	−2.8103	3.36
$1a_1 2a_1 1e$	$^2E+{}^4E$	−2.7984	3.52
$1a_1^2 3e$	^2E	−2.7949	3.57
$1a_1 2a_1^2$	$^2A_1$	−2.7865	3.69
$1a_1 1e 2e$	$^2A_1+{}^2A_2+{}^2E+{}^4A_1+{}^4A_2+{}^4E$	−2.6441	5.62
$1a_1 2a_1 2e$	$^2E+{}^4E$	−2.6322	5.79
$1e^3$	^2E	−2.5632	6.72

Table IV are used. The configurations which contain these lowest terms are: $1a_1^2 2a_1$, $1a_1 1e^2$, and $1a_1^2 1e$ for $^2A_1$, $^4A_2$, and ^2E symmetries, respectively. It should be noted that the A_1 configuration does not contain an *E*-symmetry orbital; hence, the corresponding MO calculation does not yield any information concerning these orbitals. Thus it is necessary to select a set of *E* orbitals from one of the other MO calculations in order to obtain all of the configurational terms of A_1 symmetry. The selection of these orbitals is discussed later. The values of Roothaan's parameters[21] (f, a, b) are listed in Table V for each of the configurational terms for which the MO calculations are performed.

For each MO calculation, Roothaan's equations are solved for different sets of the exponential variational parameters. The optimum set for a particular MO is determined by minimizing the corresponding energy. These minimum MO energy levels in rydbergs are $E(^2A_1) = -1.9018$, $E(^4A_2) = -1.9497$, and $E(^2E) = -1.9620$. The corresponding optimum exponential parameters and linear coefficients are shown in Tables VI and VII, respectively. A comparison of the exponential parameters of Table VI with those obtained from the one-electron calculations (Table II) shows that the MO results generally yield more diffuse orbitals, as expected, because of the electronic Coulomb repulsion.

C. Configuration-mixing calculations

The configuration-mixing calculations are carried out for the doublet and quartet states of each symmetry using the MO results contained in Tables VI and VII. As noted previously, the MO calculation for the lowest A_1 term does not yield any information for the *E* orbitals. The orbitals obtained from the A_2 MO calculation result in slightly lower energies for the A_1 configuration-mixed states, so that these orbitals are considered the appropriate set. Table VIII summarizes the admixtures [squares of the linear coefficients in Eq. (10)] of the ten lowest configurations obtained for all configuration-mixed states which are within 3.0 eV of the ground state. The corresponding calculated energy-level scheme is shown in Fig. 2. Included in Fig. 2 are the measured *R*-band energies.

The ground state is found to have ^2E symmetry, which agrees with Silsbee's assignment.[12] In addition, the admixtures of the configurations for which the MO calculations are performed are relatively large for the lowest state of the respective symmetries. This indicates that the MO results constitute a relatively accurate representation of these states even before configuration mix-

TABLE V. Roothaan's parameters for lowest-energy configurational terms for *R* center in KCl.

Configurational term symmetry	*f*	*a*	*b*
$^2A_1$	$\frac{1}{2}$	0	0
$^4A_2$	$\frac{1}{2}$	1	2
^2E	$\frac{1}{4}$	0	0

TABLE VI. Optimum molecular-orbital exponential parameters for R center in KCl.

	A_1 orbitals		E orbitals	
Lowest $^2A_1$ state	Basis function	ζ		
	s	0.405		
	p	0.456		
	d	0.680		
Lowest $^4A_2$ state	Basis function	ζ	Basis function	ζ
	s	0.499	p	0.363
	p	0.626	d_1	0.340
	d	0.975	d_2	0.520
Lowest ^2E state	Basis function	ζ	Basis function	ζ
	s	0.444	p	0.342
	p	0.673	d_1	0.280
	d	1.050	d_2	0.505

ing is performed. Figure 2 indicates that the computational results are able to predict all of the observed R bands with the possible exception of the transition to the lowest state of $^2A_1$ symmetry (R_M band).

D. Magneto-optical parameters

The calculated spin-orbit constants and orbital g values are presented in Table IX, along with theoretical and experimental values obtained by other

TABLE VII. Linear coefficients for eigenvalues of molecular orbitals for R center in KCl.

Lowest $^2A_1$ state

	A_1 orbitals			
k	ϵ_k	C_{sk}	C_{pk}	C_{dk}
1	−0.3380	0.9985	−0.0555	0.0010
2	−0.0764	0.0530	0.9484	−0.3126
3	0.4180	0.0165	0.3122	0.9499

Lowest $^4A_2$ state

	A_1 orbitals				E orbitals			
k	ϵ_k	C_{sk}	C_{pk}	C_{dk}	ϵ_k	C_{pk}	C_{d_1k}	C_{d_2k}
1	−0.5566	0.9316	−0.3406	0.1267	−0.3170	0.9723	0.1538	0.1760
2	0.0637	0.3630	0.8882	−0.2817	−0.0155	−0.1029	0.9578	−0.2685
3	0.7457	−0.0166	0.3085	0.9511	0.1156	−0.2098	0.2429	0.9471

Lowest ^2E state

	A_1 orbitals				E orbitals			
k	ϵ_k	C_{sk}	C_{pk}	C_{dk}	ϵ_k	C_{pk}	C_{d_1k}	C_{d_2k}
1	−0.3811	0.9757	−0.2017	0.0859	−0.2764	0.9579	0.0932	0.2716
2	0.2349	0.2162	0.9503	−0.2239	−0.1476	−0.0125	0.9585	−0.2850
3	0.9834	−0.0365	0.2371	0.9708	−0.0585	−0.2868	0.2696	0.9193

TABLE VIII. Admixtures of ten lowest configurations for electronic states of the *R* center in KCl. The admixtures are the squares of the linear configurational coefficients. The tabulated numbers do not add up to unity since not all of the configurations considered are listed.

Symmetry type	Energy (eV)	$1a_1^2 1e$	$1a_1^2 2a_1$	$1a_1^2 2e$	$1a_1 1e^2$	$1a_1 2a_1 1e$	$1a_1^2 3e$	$1a_1 2a_1^2$	$1a_1 1e 2e$	$1a_1 2a_1 2e$	$1e^3$
$^2A_1$	0.43		0.745		0.075			0.037	0.009		
	2.15		0.142		0.491			0.211	0.009		
	2.94		0.001		0.272			0.600	0.001		
$^2A_2$	1.47				0.786				0.023		
	2.57				0.038				0.860		
	2.99				0.016				0.600		
^2E	0.00	0.924		0.000	0.003	0.007	0.000		0.014	0.003	0.012
	1.28	0.002		0.309	0.612	0.005	0.001		0.001	0.007	0.000
	2.06	0.001		0.607	0.284	0.008	0.016		0.000	0.004	0.000
	2.62	0.000		0.019	0.004	0.214	0.583		0.086	0.008	0.012
$^4A_1$	2.58								0.936		
$^4A_2$	0.55				0.977				0.001		
	2.02				0.002				0.963		
^4E	2.35					0.908			0.070	0.001	
	2.89					0.066			0.630	0.007	

investigators. The spin-orbit constant is calculated from Eq. (24), where the matrix elements of ξ for the K^+ and Cl^- ions are listed in Table X. The orbital g value is calculated from Eq. (29) in which the free-ion energies of Clementi[26] are employed.

The molecular orbitals are orthogonalized to the core orbitals for a set of 61 ions about the defect (cube of 64 ions centered at the defect minus three vacancies). The resulting overlap integrals are linear combinations of overlaps between STO's with different origins. Procedures for calculating these quantities have been developed by Mulliken *et al.*[27] and by Lofthus.[28] In the present work, the nearest-neighbor separation is taken as 5.95 atomic units.

TABLE IX. Magneto-optical parameters for the *R* center in KCl. The reduced parameters are denoted by a subscript *R*. The measured coupling constants are denoted by k^2.

	λ_E (cm^{-1})	g_{oE}	λ_R (cm^{-1})	g_{oR}	k^2
K & S[a]	−4.8	1.1	(−0.33)	(0.075)	3.0
S[b]	(−5.4)[h]	(1.0)	−0.32	0.06	3.2
B[c]	(−5.3)	(1.2)	−0.24	0.055	3.6
MA & D[d]	(−2.4)	(0.28)	−0.70	0.080	1.1
B, M & MA[e]	(−2.5)	(0.60)	−0.64	0.15	1.25
K & S[a]	−2.1[i]	0.48[i]			
M & MB[f]	−3.63[i]	0.30[i]			
M & M[g]	−8.01[i]	0.59[i]			
Present	−10.8[i]	0.99[i]			

[a] D. C. Krupka and R. H. Silsbee, Ref. 12.

[b] I. W. Shepherd, Ref. 8.

[c] W. Burke, Ref. 9.

[d] Y. Merle-D'Aubigne and P. Duval, Ref. 10.

[e] G. Binet, J. Margerie, and Y. Merle-D'Aubigne, Ref. 11.

[f] J. Margerie and F. Martin-Brunetiere, Ref. 20.

[g] A. Maisonneuve and J. Margerie, Ref. 19.

[h] Parentheses indicate that parameters are calculated by us from experimental values using the Ham reduction factor [F. S. Ham, Phys. Rev. 166, 307 (1968)].

[i] Theory.

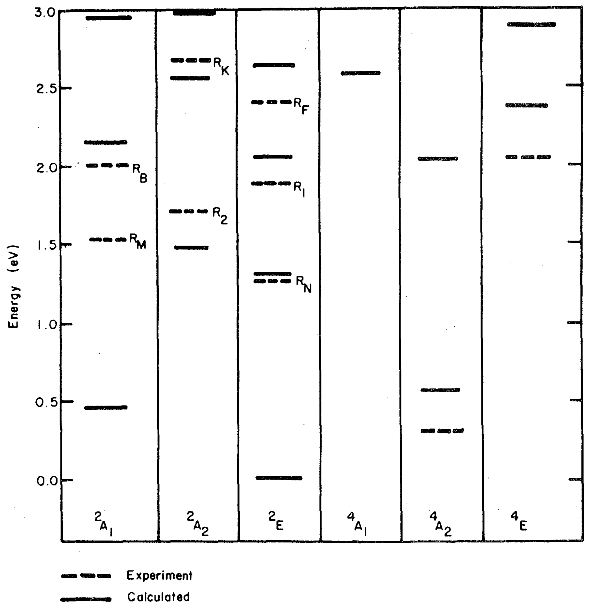

FIG. 2. Energy levels for the *R* center in KCl. Solid lines represent calculated energies while dashed lines are energies inferred from experimental data reported in Refs. 2–6.

V. DISCUSSIONS AND CONCLUSIONS

The electronic structure of the *R* center in KCl has been investigated theoretically by an open-shell molecular-orbital calculation with configuration mixing. The calculated results have been used to identify the excited states which are associated with each of the observed bands. Calculated and measured transition energies agree well; only the $^2A_1$ state exhibits a large quantitative difference with experiment. These results give further confirmation of the symmetry assignments for the bands made on the basis of experiment.

Although the present work has yielded wave functions which prove useful in preliminary calculations of the properties of the *R* center, these wave functions are subject to further refinement. It is noted that static-lattice distortion is omitted in this treatment. Ion-size effects should be included in the electronic-structure calculation.[29] A further refinement of the present treatment would be the expansion of the basis set to include *f* orbitals. This would permit azimuthal variation of the molecular orbitals and provide A_2-symmetry one-electron orbitals.

TABLE X. Matrix elements of the spin-orbit operator (in electron volts).

	$\zeta_{\alpha 2p2p}$	$\zeta_{\alpha 3p3p}$	$\zeta_{\alpha 2p3p}$
K^+	1.874	0.158	−0.531
Cl^-	1.096	0.062	−0.254

The wave functions described above have been employed in a calculation of the ground-state magneto-optical parameters λ_E and g_{oE}. It is difficult to obtain an accurate value for λ_E, since the value of this parameter depends on cancellation of large ionic contributions [Eq. (24)]. It is noted that the magnitude of the calculated spin-orbit constant is greater than even the largest experimental value. We believe that this is a consequence of neglecting extended-ion effects and lattice relaxation in the electronic-structure calculation. A more diffuse wave function would tend to reduce the magnitude of λ_E.

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