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Calculation of the electronic structure of color centers by the multiple-scattering method*

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The electronic structure of the U, F, U_1, and U_2 centers in KCl has been studied using the self-consistent multiple scattering (or scattered wave) $X\alpha$ method. In these calculations, clusters including the first-nearest neighbors are used to find the peak energies of various absorption bands. The calculated energies for the U and F centers agree well with the experiment. In the case of the U_2 center, two possible transitions are investigated and one agrees well with the experimental value while the other, a charge-transfer process, gives an energy too small. The hyperfine interaction of the U_2 center and the optical absorption of the U_1 center have also been studied.

INTRODUCTION

F, U, U_1, and U_2 centers are the simplest color centers that can occur in alkali halides and they are good test examples for our initial theoretical approach toward the understanding of the electronic structure of color centers. We have chosen KCl for our calculations because of the availability of a large amount of experimental data on all of these centers. The experimental techniques which have been applied include optical spectroscopy, electron paramagnetic resonance (EPR), and electron-nuclear double resonance (ENDOR).[1-5] From the experimental results, especially EPR and ENDOR, the structures of the centers can be deduced. The F center is an electron trapped in an anion vacancy in the alkali-halide crystal. The U center is believed to be a negative hydrogen ion substituted for an anion in the crystal. The U_1 and U_2 centers are interstitial defects. The U_1 center is believed to be a negative hydrogen ion in an interstitial site of the crystal and the U_2 center, a hydrogen atom in the same site.

Many theoretical calculations of the F center have been carried out. A summary of various methods applied up to 1960 can be found in the article by Gourary and Adrian.[6] We can see that most of the works before 1957 use semiempirical techniques. There are other methods using variational techniques like the point-ion approximation.[7] More extensive semiempirical calculations have been carried out by Wood and Joy,[8] Kubler and Friauf.[9] A discussion of these works and other calculations is given by Fowler.[10] (For more recent calculations on F centers see Refs. 11, 12, 46, and 47.) Since the U center has the same point symmetry as the F center, calculations of the U center[13,14,48] have employed the same methods that were developed for the F center. As for the U_1 center, there have been no theoretical calculations, partially because it has no interesting magnetic properties (the ground state is a closed shell) and partially because the peak of the U_1 band in the absorption spectrum is generally not well defined.[1,15] Contrary to the case of the U_1 center, a great deal of work has been done on the U_2 center.[16-18] Kerkhoff, Martienssen, and Sander[19] examined various possibilities of the optical process for the U_2 center in a semiclassical way, and concluded that the optical U_2 band is due to a charge transfer from the nearest-neighbor halogen ions to the hydrogen atom. The configuration of the excited state of the U_2 center is thought to be a negative hydrogen ion plus a hole in the p orbitals of the nearest-neighbor halogen ions. Using these configurations, Cho *et al.*,[20,21] obtain the wave functions to discuss the hyperfine interaction. Other calculations involving the variation technique has been done by Sammel.[22] Calculations of the transition energy of the U_2 band have been done semiempirically by Hagston[23] and Schechter[24] and earlier by Mimura and Uemura.[16]

In this work, we have calculated mainly the optical transition energy of the F, U, U_1, and U_2 centers in KCl including the first-nearest-neighbor ions by using the self-consistent multiple-scattering $X\alpha$ method. Discussions of the hyperfine interaction and effects of lattice distortion are given in later sections.

CALCULATIONS

The self-consistent multiple-scattering $X\alpha$ method was developed by Johnson[25-27] and has been successfully applied to many molecular systems,[28-30] and cluster models of impurities in crystals.[31] In the present calculation, we use a model cluster, which consists of a central ion (or a trapped electron) and its first nearest neighbors, to study the electronic structure and optical absorption processes of the color center.

To simplify the multiple scattering method, we

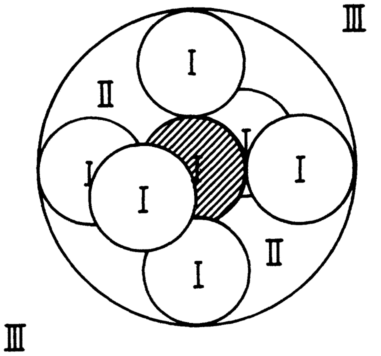

FIG. 1. Multiple-scattering model for U and F center showing schematically the atomic spherical region I, outer sphere region III, and the interstitial region II.

have used the muffin-tin approximation in which the potentials and charge densities in the spheres containing the ions and in the space exterior to an outer sphere that encloses the whole cluster are spherically averaged. For the region between the ion spheres and the outer sphere, volume averages of the charge density and potential are used. Figure 1 shows schematically this division of space.

In an ionic crystal, each ion forms a closed shell system. From the x-ray diffraction experiment,[32] the electronic charge distributions of ions in an ionic crystal are very nearly spherically symmetric. Thus, the muffin-tin approximation used in the present case is considered to be appropriate.

The $X\alpha$ statistical exchange[33,34] has been used in the equations satisfied by the one-electron orbitals. The α value used for the K^+ ions and for the Cl^- ions is chosen to be 0.72 which is close to the values from Schwarz' calculations of the optimum values for the atomic case.[35] As for the hydrogen atom or hydrogen ion, the α value is 0.77 for a spin-polarized atomic calculation.[36,37] We also use a weighted average for the intersphere and outer region. Since the best α values for the various regions in the crystal calculation are not known and since the variation of α from atom to ion is not significant, we feel that the above choices can best reflect the abilities and limitations of the present form of the multiple scattering method.

In the beginning of this investigation, we used the commonly used ionic radii[38] for the radii of ion spheres in which the K^+ sphere has a radius of 2.51 au (1.33 Å) and the Cl^- sphere has a radius of 3.42 au (1.81 Å). However, in order to make the best use of the muffin-tin approximation, we have attempted to find a set of radii which can better represent the relative sizes of ions in the crystal.

There are a few experiments employing x-ray diffraction techniques which can determine the electron charge distributions of ionic crystals.[32,39] A set of corrected ionic radii has been deduced by Gourary and Adrian[6] from the x-ray diffraction data. Using the corrected ionic radii, which are 2.82 (1.49 Å) and 3.10 au (1.64 Å) for the K^+ and Cl^- ions, we find that the potentials and radial charge densities of the two ions at the point of contact of their respective spheres are approximately equal. We also notice that there is more charge inside the ionic spheres and less in the intersphere region.

In all calculations except the U_2 center, the cluster that we used is not neutral. The environment of the cluster was simulated by the use of a Watson sphere,[40] equal to the outer sphere and carrying a charge equal and opposite to that of the cluster. Presumably, this charged sphere also gives the right correction for the potential inside the cluster, and usually the cluster properties are insensitive to the charge on the Watson sphere.[31] Calculations have been carried out using this correction for all centers. Later, we found that since the U- and F-center clusters use a charged sphere with charge -5 and the radius of this charged sphere is normally chosen to be the same as that of the outer sphere, the potential compensation inside the cluster, which is equal to $-10/R$ Ry (R is the radius of the outer sphere), is quite sensitive to the choices of the radii of the ion spheres used. Therefore a more accurate potential correction inside the cluster which is dependent only on the nearest-neighbor distance in the ionic crystal is needed. A volume-averaged point-ion potential inside the outer sphere but excluding the space occupied by the surrounding ions has been calculated. This potential correction is approximately equal to $-7.9/a$ Ry, where a is the nearest-neighbor distance, with small deviations due to the variations of the volume of the cluster using different relative sizes of the ion spheres.

In finding the optical excitation energy of various centers in this paper, we have used the "transition state" concept[26,41] in which the electron occupation numbers are chosen to be halfway between the initial ground state and the final excited state. The excitation energy of the transition can be found by taking the difference of the two one-electron spin orbital energies that are involved in the transition.

RESULTS

A. U center

We have calculated the electronic structure and the peak energy of the absorption band of the U center in KCl using a cluster consisting of a H^-

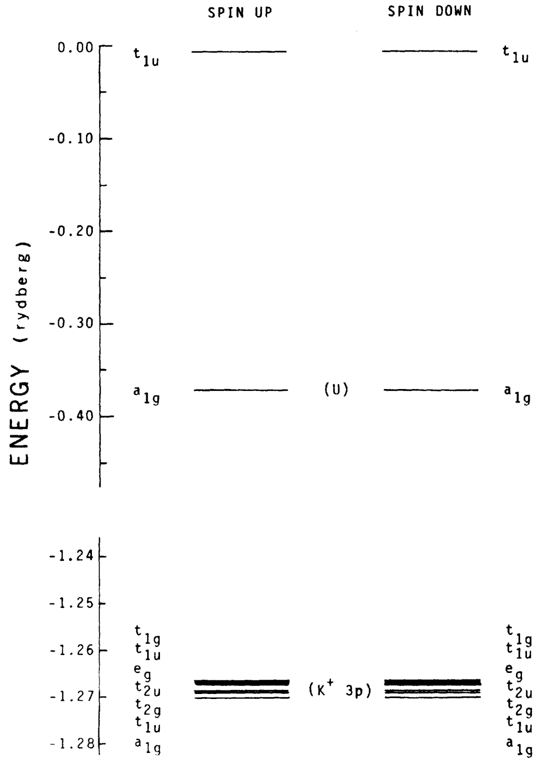

FIG. 2. Ground-state orbital energies of the *U* center in KCl calculated by using the $H^-(K^+)_6$ cluster.

TABLE I. Calculated optical absorption energies and electronic charge distribution from several transition state calculations of the *U* center in KCl. All energies are in Ry and distances are in a.u. Experimental value of $\Delta E = 0.426$ Ry.[a]

	Av. point-ion correction		Charged-sphere correction	
	XR	OR	XR	OR
$V_I(r \le R_{\mathrm{out}})$	1.335	1.335	1.141	1.184
R_{out}	8.768	8.448	8.768	8.448
R_{H^-}	3.100	3.420	3.100	3.420
R_{K^+}	2.834	2.514	2.834	2.514
ΔE	0.427	0.417	0.458	0.438
$\epsilon(a_{1g})$	−0.488	−0.497	−0.653	−0.628
$\epsilon(t_{1u})$	−0.061	−0.080	−0.195	−0.190
Q_{int}	1.240	2.157	1.350	2.200
Q_{H^-}	1.410	1.509	1.439	1.540
Q_{K^+}	17.846	17.680	17.850	17.680
Q_{out}	0.270	0.255	0.091	0.138

[a] J. W. Schulman and W. D. Compton, *Color Center in Solids* (Macmillan, New York, 1962).

ion at its center and six nearest-neighboring K^+ ions (see Fig. 1). The nearest-neighbor distance of this cluster is kept the same as that of a pure KCl crystal at equilibrium. Several calculations with different sets of radii and different correction potentials have been tried. The orbital energy levels of one ground-state calculation, which uses the Gourary and Adrian's x-ray corrected radii (XR)[6] and the averaged point-ion potential, are shown in Fig. 2. No spin-polarization effect appears in the eigenvalues in this spin-unrestricted calculation. This is expected from a system consisting of closed shell ions. The hydrogen 1*s* level appeared as two a_{1g} symmetry orbitals, one with each spin. These two a_{1g} levels are well localized in the central part of the cluster as the calculated result showed that 85% of the electronic charges of these orbitals are within the central sphere and the rest of the charge is distributed mostly in the intersphere region. Below the hydrogen levels, the next occupied levels are a group of several levels for each spin that arise from the atomic 3*p* levels of the six K^+ ions. These levels are relatively deep compared to the hydrogen a_{1g} orbital and their charges are concentrated in the K^+ spheres. Hence, only a relatively small interaction is expected between this group of levels and the hydrogen levels. The optical absorption process in this case is expected to be an electron excited from the hydrogen a_{1g} level to the next higher allowed level, which is a t_{1u} orbital with the same spin. By using the transition-state technique, this excitation energy can be calculated.

The results of several transition-state calculations with different sets of ionic radii and different correction potential are shown in Table I. In this table, the correction potential inside the outer sphere, various sphere radii, transition energy, eigenvalues, and the electronic charges inside each region of the cluster are given. With the averaged point-ion correction, the calculated transition energies are 0.427 and 0.417 Ry using the XR and the ordinary ionic radii (OR),[38] respectively. While with the charged Watson sphere correction, the transition energies are 0.458 and 0.438 Ry using the XR and the OR, respectively. The difference in the transition energies between the latter two calculations is doubled as compared to that in the former two. Thus, the averaged point-ion correction is a better choice to use in the present calculation.

Comparing the electronic charges in each region, one finds that the major difference in using the XR as compared to the OR is that there is less electronic charge in the intersphere region. The XR seem to give a better representation of the size of the ions in crystal. In any case, if one compares the calculated transition energies with the experimental absorption energy, one finds that the present calculated values are very close to the observed value with the largest deviation being about 7%. The best agreement occurs when we use the averaged point-ion correction and the XR. In this case, the calculated transition energy is almost equal to the experimental value. In a more complete investigation,[42] a similar problem has been studied for a number of other ionic crystals. The results show that the present approach gives good results on the *U*-center transition energies in most of the cases except in the case of the LiF crystal which has the smallest interionic distance.

There are several ways to improve the present approach; namely, the inclusion of more ions into the calculation, the relaxation of the neighboring ions near the defect center and the removal of the muffin-tin restriction. Larger clusters including the second nearest neighbors have been carried out.[42] The calculated *U*-center absorption energy was found to oscillate about the present small cluster result as shells of ions are added. The charge distribution obtained from these calculations indicated that the anion sphere, in general, contains a net charge of less than 0.4 electronic charge. The rest of the charges of the anions are mainly distributed in the intersphere region. Because of this nature of the charge distribution, the point-ion correction potential is expected to be somewhat different from the actual crystalline potential. It is believed that the error in using the point-ion correction becomes significant in the cases of larger clusters and a more accurate evaluation of the correction potential inside each region of the cluster is essential for getting quantitatively good results. The lattice distortion is relatively easy to incorporate into the small cluster calculation. An estimation has been made in which the transition energy of the *U* center in KCl increases about 0.004 Ry if the first-nearest-neighboring ions are allowed to displace inward by 1% of the interionic distance of the crystal. At present, the determination of the amount of the lattice distortion near the *U* center by fitting data to the experimental results is certainly unwarranted since there are other effects to be considered. Thus, no attempt was made in this regard. The removal of the muffin-tin approximation is expected to give more accurate results without the uncertainty in choosing the radii for the atomic spheres. The research in this direction is in progress. In any case, the present approach does give a straightforward method to study the color center in ionic crystals. The use of the muffin-tin approximation seems to be appropriate in the present *U* center case and provides results that are fairly accurate.

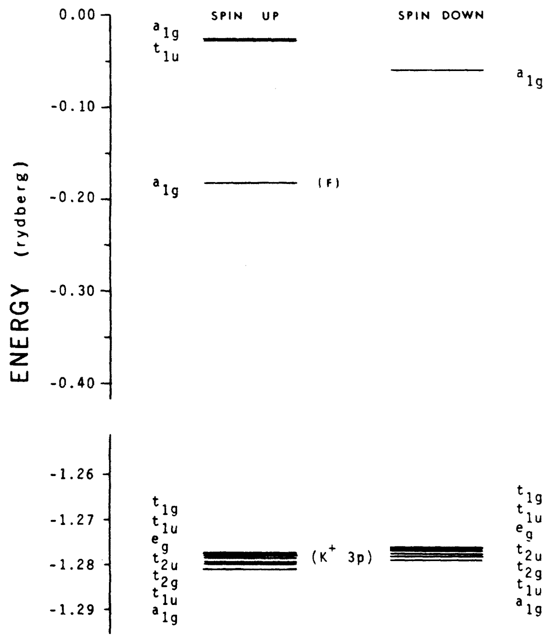

FIG. 3. Orbital energies from the ground-state calculation of the *F*-center cluster.

B. *F* center

The *F*-center calculation proceeds the same way as the *U*-center calculation except that only an electron is left in the center of the cluster. The value used for the local exchange term is 0.72 everywhere. Also, the averaged correction potential and XR are used in the calculation. The ground state of the *F*-center cluster in KCl has been calculated and the orbital energies are shown in Fig. 3. In this case, the spin-polarization effect caused by the unpaired electron is clearly shown in the diagram. The occupied *F*-center a_{1g} level is at -0.183 Ry and the probability for this electron in the central-sphere region is about 0.517 and the probability in the intersphere region is 0.357. Thus, the *F*-center ground-state orbital is localized in the anion vacancy although it is not as localized as the *U*-center orbital. On the other hand, the first allowed excited state of the *F* center (which is a t_{1u} orbital with spin up at -0.029 Ry) is relatively extensive. The probabilities for an electron is this orbital in the intersphere region and outer region of the present cluster are 0.464 and 0.432, respectively.

From the transition-state calculation, the excitation energy is found to be 0.173 Ry which is in excellent agreement with the experimental value (0.169 Ry). We also tried to use the *F*-electron wave function from the ground-state calculation to compute the contact term for the spin interaction between the *F*-center electron and the neighboring ions. This term turns out to be much higher than the experimental value.

The possible improvements for the *F*-center calculations are similar to the ones that are discussed in the previous *U*-center section. It is believed that a larger cluster and an accurate potential can give a better result on the form of the *F*-center wave function.

C. U_2 center

The calculation of the U_2 center in KCl has been done using the cluster shown in Fig. 4. In this cluster a hydrogen atom is surrounded by four K^+ ions and four Cl^- ions. Since this cluster is electrically neutral, no Watson sphere is needed in this case. The parameters used are the same as those used in the *U*-center calculation except for the radius of the interstitial hydrogen sphere which is chosen to be as large as possible without overlapping the other spheres. By this criterion, the radius of the hydrogen sphere is 2.04 au.

The orbital energies of the ground state of this cluster are shown in Fig. 5. The hydrogen 1*s* state is an a_1 orbital with spin up in the present T_d symmetry environment. The $1a_1$ and $2a_1$ orbitals with spin up are mixed states from both the hydrogen and the neighboring Cl^- ions. From the charge distribution of the orbitals, it is found that the most hydrogenlike a_1 orbital with spin up is below the group of levels from the Cl^- 3*p* states. On the other hand, the unoccupied hydrogen-like a_1 orbital with spin down is above the chlorine levels. Thus, in this spin-unrestricted calculation, we know that the system with two electrons in the hydrogen states plus a hole in the chlorine 3*p* levels has a higher energy than that which has filled chlorine 3*p* levels and one electron in the hydrogen level. This situation was unclear from the energy consideration of Cho *et al.*,[20] although the same conclusion was reached.

In finding the excitation energy of this center, there are two possible forms of transition. The first possibility is an electron excited from the $2a_1$ orbital with spin up, which is a mixture of hydrogen 1*s* level and the Cl^- 3*p* levels, to the unoccupied $3t_2$ orbital. The second possible form of excitation is to excite an electron from the spin down $2t_2$ orbital, which is an orbital concentrated on the four Cl^- ions, to the unoccupied hydrogen $2a_1$ orbital. The transition energies calculated from these two kinds of transition are 0.395 and 0.213 Ry, respectively. Comparing these results with the experimental U_2 center absorption energy in KCl (0.387 Ry),[43] the first form of transition is found likely to be the actual process. In most of the previous calculations on optical transitions in a U_2 center,[16,23] the absorption process was thought to be a charge transfer which is equivalent to the second form of transition in the present calculation. In order to see the effect of

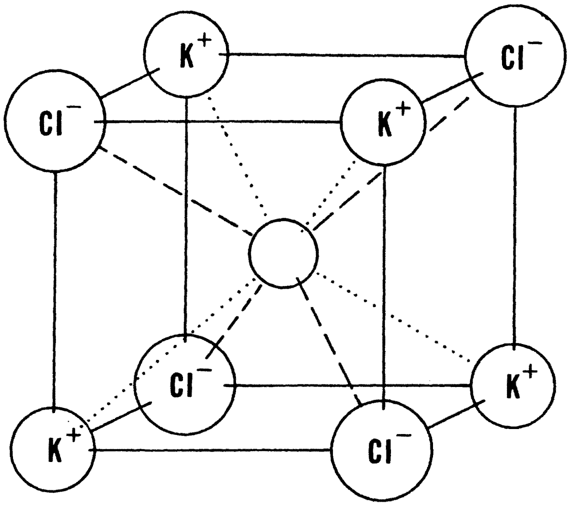

FIG. 4. Cluster used in the U_1- and U_2-center calculations.

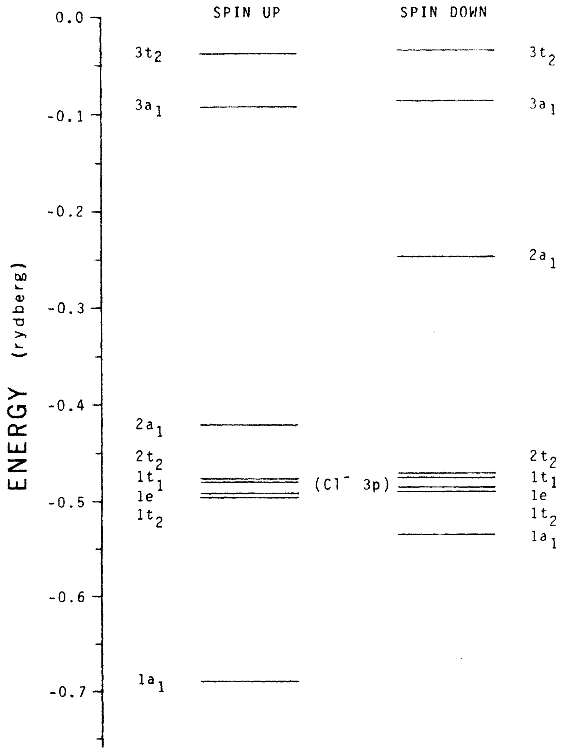

FIG. 5. Orbital energies from the ground-state calculation of the U_2-center cluster.

the possible lattice distortion around the hydrogen atom upon the transition energy, a calculation of the charge-transfer process with the Cl^- ion and the K^+ ion displaced outward and inward, respectively, along the line joining the ion and the hydrogen atom was carried out. The result shows an even smaller energy for the U_2 center absorption. Thus, from the present calculation the process of charge transfer cannot account for the U_2 absorption energy, and the process with an electron excited from a hybrid chlorine-hydrogen a_1 orbital to a higher state gives a good interpretation of the absorption. The absorption of the charge transfer process may be masked by the nearby *F*-center absorption band.

The proton hyperfine interaction of the U_2 center in KCl has been investigated by many workers in this field. Spaeth and Seidel[17] used the orthogonalized function method and obtained a relative proton hyperfine constant shift $\delta = 9.27\%$, where δ is defined by

$$\delta = (a_{H_i} - a_H)/a_H \tag{1}$$

and a_{H_i} is the proton hf constant for the U_2 center (an interstitial hydrogen atom) while a_H is the hf constant for a free hydrogen atom. Since the experimentally determined a_{H_i} (1378 MHz) is less than the free hydrogen hf constant (1420 MHz), the relative proton hf constant shift is equal to -3.01%.[44] To improve the calculated values, they tried to take into account the Van der Waals interaction between the H atom and its neighboring ions. This has the effect of shifting electron density away from the proton into the outer region of the H atom resulting in a value of $\delta = -9.73\%$. Another model to improve the calculation of δ is to include the crystal field effects using the ligand field model. In this way, Hagston[18] obtained a value of δ between -1% and -2% in a semiempirical calculation.

In the present calculation, the proton hf constant is calculated from the spin density at the position of the proton which can be calculated from the following expression:

$$\rho(\vec{r}) = \sum_{i(\uparrow)} n_i |\Psi_{i\uparrow}(\vec{r})|^2 - \sum_{j(\downarrow)} n_j |\Psi_{j\downarrow}(\vec{r})|^2 , \tag{2}$$

where n_i is the occupation number of the ith state and $\Psi_{i\uparrow}(\vec{r})$ is the wave function of the ith state at position $\vec{r}$. The summation of i is over all states with spin up and the summation of j is over all states with spin down. Using the spin density at the proton, the calculated δ is equal to -4.5% which is in fairly good agreement with the experimental value.

The calculation of the hf contact term at the nuclei of the Cl^- and K^+ ions has also been done using the spin density obtained from Eq. (2). Comparing with the experimental results the calculated hf contact term for the Cl^- ion is overestimated and that for the K^+ ion is underestimated and is negative. In order to see the effect on the distribution of the spin polarization due to a particular choice of the cluster, a different cluster for the U_2 center in KCl was used. This cluster has a K^+ ion at the origin with six Cl^- ions surrounding it and also has a hydrogen atom located at $(\frac{1}{2}d, \frac{1}{2}d, \frac{1}{2}d)$ of the cluster, where d is the nearest-neighbor distance of the crystal. This cluster has C_{3v} symmetry. The calculated hf contact term for the K^+ ion in this case is improved and has a value near zero. The hf contact term for the Cl^- ion is lowered. Thus, overall the cluster with C_{3v} symmetry has improved results for the hf contact term compared to the tetrahedral cluster, but the results are not satisfactory. In the present calculation the spin polarization is mainly within the outer sphere of the cluster in contrast with the experimental results that show spin polarization in the third shell of ions. A larger cluster may be used to improve the results. On the other hand, the hf contact term of the nearest-neighbors of the interstitial hydrogen can also be calculated approximately using the one-electron wave function of the unpaired electron from the tetrahedral-cluster calculation. The hf contact term at the Cl^-

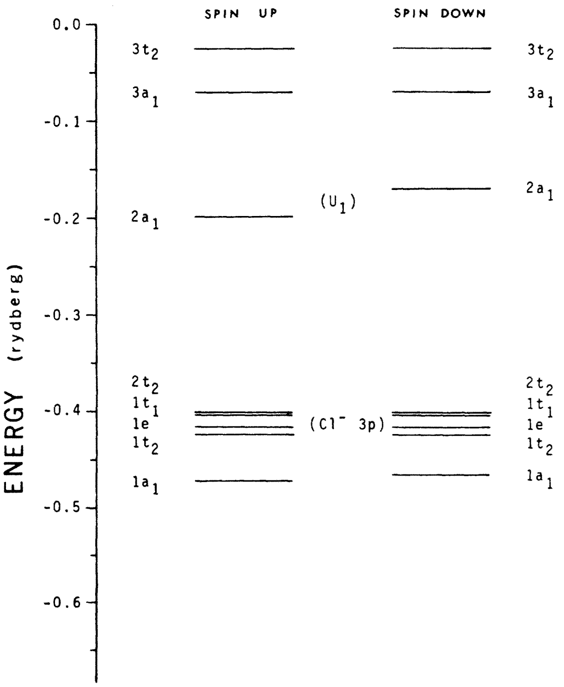

FIG. 6. Orbital energies from the ground-state calculation of the U_1-center cluster.

nucleus in the first shell is found to be 18.0 MHz which is roughly comparable to the experimental value of 23.7 MHz. At the K^+ nucleus, the calculated hf contact term is 3.1 MHz and the experimental value is 1.0 MHz. These results are better than the results obtained using Eq. (2). But the calculated spin density at the proton position using the one-electron wave function is found to be too small. The reason for this low spin density is probably the fact that the hydrogenlike a_1 orbital is mixed with the a_1 orbital from the neighboring Cl^- ions shifting the spin density away from the proton.

D. The U_1 center

The U_1 center is similar to the U_2 center discussed in the previous section except that the interstitial impurity is a negative hydrogen ion in the present case. The study of this center in KCl has been done using the tetrahedral cluster shown in Fig. 4. A Watson sphere with charge of +1 was used to enclose the whole cluster.

The calculated orbital energies are shown in Fig. 6. Contrary to the case of the U_2 center, both of the two hydrogenic $2a_1$ orbitals are above the group of five levels arising from the Cl^- $3p$ levels. The optical absorption process in this case is thought to be an electron excited from the hydrogenic $2a_1$ orbital to the first unoccupied $3t_2$ orbital. The transition state calculation has been done and shows a transition energy of 0.18 Ry. There are a few experimental measurements of the absorption band of the U_1 center in KCl,[1,15] but the peak of this band generally is not clearly defined. It is estimated that the peak of the absorption band is at about 0.32 Ry and the edge of this band is about 0.26 Ry.

In the case of this interstitial impurity, the interaction between the hydrogen ion and the neighboring ions is believed to be greater than that of the previously discussed centers. Consequently, the displacement of ions with respect to their equilibrium positions is more important. Thus, two more calculations with displacements were carried out. In these calculations, the chloride ions were allowed to displace outward along the cubic diagonals and the potassium ions were allowed to displace inward along the cubic diagonals. The hydrogenlike level was found to shift down because of the relaxation of ions surrounding it, and the resulting transition energies were 0.22 and 0.25 Ry with the ions displaced approximately 5% and 8% of the nearest-neighbor distance form their crystal equilibrium positions, respectively.

Thus, from the above results, we know that the displacement of the neighboring ions of the hydrogen plays an important role in the U_1 center structure. Since the actual amount of displacement or other distortions of the crystal lattice are not known, we can only qualitatively understand the problem. For more accurate calculations, the polarization effect due to the extra electron on the hydrogen and the more general form of potential must be considered.

DISCUSSION

We have applied the multiple scattering method to several color-center problems. In general, the ground-state orbitals of these color centers are found to be quite localized and are mainly in the central part of the cluster, while the excited-state wave functions are found to be more extended and are in the intersphere region and the outer region. Because of the ionic nature of the KCl crystal, the energies of these two states are affected by the crystalline potential differently. Thus, in finding the transition energies of various cases, the proper correction potential for the cluster is essential.

For the present small cluster calculation, the U-center and F-center results agree well with the observed values. In a similar cluster calculation of the pure KCl crystal[42] in which a Cl^- ion is surrounded by six K^+ ions, the calculated energy gap is also in good agreement with the experimental value. The exceptionally good results obtained in the case of the KCl crystal, as mentioned before, are accidental in view of the averaged correction potential and other approximations. But the consistency in predicting transition energies in several different centers does imply that the present cluster calculation may also be used semiempirically. This can be done by comparing the calculated energy gap with the experimental data or other accurate energy band calculations to determine the correction potential needed for a particular cluster in any crystal. With this information, the defect problem can be studied with good accuracy. At present, the averaged point-ion correction potential used for the small cluster calculation is found to be adequate for a number of cases except the crystal with the smallest interionic distance. Thus, the semiempirical procedure has not been used.

In finding the hyperfine interaction between the unpaired electron and the neighboring ions, the results are, in general, not satisfactory. This is probably due to the relatively small cluster being used in the calculation.

From our experience with the multiple-scattering $X\alpha$ method we realize that a small cluster for a point defect in ionic crystals is enough to take into account optical transitions. If we use a larger cluster the optical transitions are going to be similar, but to calculate the hyperfine interaction, we need to consider a larger cluster to get the correct spin-polarization because the wave functions in the outersphere region usually decay too rapidly.[42,45]

In conclusion, we think that the present method is suitable for studying the color-center problem and other impurity problems in solid. It represents an improvement over other calculations, since it deals explicitly with the electronic structure of the nearest-neighbors. It also includes the exchange interaction (through the use of the $X\alpha$ exchange potential) and is a self-consistent method. The major limitation of the present form of the multiple scattering method is the assumption of a muffin-tin potential. In the case of a substitutional center, the electronic charge in the intersphere region is found to be very small. This indicates that the muffin-tin potential is a good approximation. On the other hand, in the case of an interstitial center, the charge densities of the hydrogen ion are believed to overlap with the neighboring ions. Thus, the muffin-tin form of the potential will introduce some errors, as we have experienced in the U_1 center calculation.

Study of the large cluster calculation is in progress. It is found that a more accurate evaluation of the correction potential becomes necessary in the large cluster case in order to give satisfactory results. These calculations can be applied to the more complicated color-center problems.

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