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Electronic structure and optical properties of the impurity Cu^+ in NaF

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The electronic structure of the impurity Cu^+ in a sodium fluoride crystal has been studied using the ICECAP (ionic crystal with electronic cluster, automatic program) methodology, which treats the defect and its vicinity quantum mechanically as a molecular cluster embedded in a shell-model lattice. The electrons in the cluster have been treated in the unrestricted Hartree-Fock self-consistent-field approximation, corrected for correlation by use of the many-body perturbation theory. The surrounding infinite lattice has been described by the shell model that incorporates host polarization and distortion self-consistently. The basis sets used to describe the Cu^+ ion were optimized. The excitation energy and the crystal-field splitting were computed as 4.02 and 0.31 eV, respectively, versus the corresponding experimental results of 4.20 and 0.35 eV, respectively.

I. INTRODUCTION

The Cu^+ ion in alkali halides has been an interest to both experimentalists and theoreticians for many years. Payne *et al.*[1,2] made elaborate measurements on the Cu^+ impurity in NaF and some alkali chlorides. The separation of the $\Gamma_1\ (d^{10}) \rightarrow {}^1\Gamma_{12}\ (d^9s)$ transition from the overlapping $\Gamma_1\ (d^{10}) \rightarrow {}^1\Gamma'_{25}\ (d^9s)$ transition was determined using two-photon polarized spectra. Many theoretical studies use finite cluster models in which the lattice distortion and polarization are not counted effectively. In the ICECAP (ionic crystal with electronic cluster, automatic program) (Ref. 3) methodology, the surrounding lattice is allowed to respond self-consistently to the charge distribution of the defect cluster.

ICECAP (Ref. 3) is a result of collaboration among groups at Michigan Technological University, the University of Manitoba, Canada, and Atomic Energy Research Establishment, Harwell, UK. Special aspects of its implementation have been described by Kunz, Meng, and Vail.[4]

We present the ICECAP methodology in Sec. II. The calculations and the results are described in Sec. III, and the conclusions are given in the final section.

II. ICECAP METHODOLOGY

The point defect and the ions that are significantly perturbed from states that they had in the perfect crystalline lattice are called the defect cluster. For the defect cluster we use the unrestricted Hartree-Fock self-consistent-field (UHF SCF) approximation, in the formalism given by Kunz and Klein,[5] augmented by a size-consistent many-body perturbation theory (MBPT) (Ref. 6) correlation correction. Adams,[7] Gilbert,[8] and Kunz[5,9–12] have discussed the formalism by which a system may be partitioned into a cluster and its environment such that the localization of orbitals in the cluster can be ensured. We solve the Hartree-Fock equation by expanding the wave function in a series of contracted Gaussian orbitals. The UHF and MBPT codes developed by Kunz and his coworkers have been used to find the Hartree-Fock energy and to perform the perturbation calculations. Application of MBPT to the finite cluster model was performed by Goalwin and Kunz.[13]

The surrounding perturbed infinite lattice is described in terms of the static shell model, which is usually adequate for harmonic lattice properties. The shell model has been widely successful in describing perfect lattice[5] and certain simple defect properties in ionic and semi-ionic crystals such as alkali halides,[14] alkaline-earth oxides,[14] and alkaline-earth sulfides.[15] In the shell model an ion is represented as a point-charge core coupled harmonically to a uniformly charged massless spherical shell of indeterminate radius. That is, ions are represented by polarizable point-charge combinations. Ions interact by means of their Coulomb and short-range shell-model potentials. The form of the short-range repulsive interaction is exemplified by the Buckingham potential of the form

$$V(r) = Be^{-r/\rho} - C/r^6 . \tag{1}$$

The defect cluster is seen by this shell-model environment as a Coulomb potential expressed as a multipole expansion and also by means of short-range interactions of ions in the defect cluster with the ions in the environment. The Coulomb potential of the defect cluster is computed directly from the quantum-mechanical charge density of the defect cluster itself.

In applying the shell-model to point defects, the Harwell automatic defect examination system (HADES),[16] as described by Norgett, divides the crystal into an inner region I and an outer region II. Beyond a specified radius R_0, defined as region IIb, HADES relaxes the ions to a configuration consistent with continuum dielectric theory, in which the lattice only sees the total charge of the defect. Inside R_0, the ionic configuration is determined by explicit energy minimization, including anharmonic (region I) and harmonic (region IIa) contributions, consistent with region IIb.

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The defect cluster embedded in a shell-model lattice is described mathematically in terms of lattice coordinates, denoted R, a set of linear basis-set coefficients in the molecular orbital (MO) formalism for the UHF SCF method, denoted C, nuclear coordinates within the defect cluster plus additional point charges, denoted R_c, and coefficients of determinants found by MBPT, denoted as A. The total energy of the defect is then E (R_c, C, R, and A), and in principle is minimized with respect to R_c, C, R, and A. In practice, however, perturbative methods determine A and direct minimization is only achieved with respect to the other variables. That is,

$$\frac{\delta E}{\delta R_c}=\frac{\delta E}{\delta C}=\frac{\delta E}{\delta R}=0 . \tag{2}$$

This results in obtaining R_c, C, R, and E as well as A. Furthermore, in this work a further level of optimization was included, namely for the set of Gaussian exponents to be used in augmenting the basis set of correlation correction.

III. CALCULATIONS AND RESULTS

The host crystal NaF has NaCl structure with octahedral site symmetry. The substitutional impurity Cu^+ in NaF is therefore surrounded by an octahedron of F^- ions.[1,2]

The parameters for the shell model and the short-range potential for the host lattice were taken from Catlow *et al.*,[17] reproducing the perfect lattice properties such as lattice energy and dielectric and elastic constants. We notice here that the nearest-neighbor distance in the lattice (2.295 Å) used in the fitting procedure is slightly smaller than the experimental value, 2.31 Å. We used the Buckingham form of short-range potential shown in Eq. (1).

Our defect cluster consists of the substitutional impurity Cu^+ and the six nearest-neighbor F^- ions, with a total of 88 electrons. The six F^- ions are to be moved in the total-energy-minimization procedure. Gaussian primitive functions are associated with Cu^+ and the six F^- ions.

TABLE I. Comparison of the orbital energies (Hartree) of free $Cu^+(d^{10})$ with those in NaF and of free Cu atom.

	Free $Cu^+(d^{10})$ (UHF)	$Cu^+(d^{10})$ in NaF (ICECAP)	$Cu(d^{10}s)$ atom (Huzinaga[a])
TE	−1638.241 965		−1638.4723
1*s*	−329.016 562	−328.627 637	−328.6400
2*s*	−41.148 003	−40.762 246	−40.7800
2*p*	−35.968 584	−35.582 285	−35.5985
3*s*	−5.342 954	−4.976 132	−4.9890
3*p*	−3.660 788	−3.295 520	−3.3049
3*d*	−0.820 667	−0.453 790	−0.4710
3*d*		−0.444 931	
4*s*			−0.2321

[a]Reference 10.

TABLE II. Exponents of the Gaussian primitives added to the basis sets for correlation corrections.

	$Cu^+(d^{10})$ and $Cu^{2+}(d^9)$	$Cu^+(d^9s)$
s		0.50
p	0.65	0.70
d	0.70	0.75
d	2.80	2.50
f	2.90	2.95
f	0.50	0.50

The contracted Gaussian-type-orbital (GTO) basis set (43,4) for F^- was chosen from Huzinaga.[18] The basis sets for $Cu^+(d^{10})$, $Cu^+(d^9s)$, and $Cu^{2+}(d^9)$ have been obtained by optimizing the contraction coefficients using the exponents of the basis sets (5333,53,5) given by Huzinaga.[18] A comparison of the orbital energies of the free $Cu^+(d^{10})$ with the $Cu^+(d^{10})$ in NaF and the free Cu atom is listed in Table I.

When the MBPT correlation correction was included in the calculation, the basis sets were augmented by some extra primitives. Considering the possible double transitions, $3d^2 \Longrightarrow p^2+d^2+f^2+g^2+pf$ and $3d4s \Longrightarrow p^2+sd+pf$, and their relative contributions to the energy, we added an extra *p*, two *d*, and two *f* to the d^{10} configuration and one more *s* to the d^9s configuration of Cu^+. The exponents of the added primitives were optimized by minimizing the total energy including correlation correction, and are listed in Table II.

The ICECAP calculations were carried out for the ground Γ_1 and excited ${}^{1,3}\Gamma_{12}$ and ${}^{1,3}\Gamma'_{25}$ states with and without MBPT. The excited states were formed by promoting one of the electrons of the $3d^{10}$ ground-state configuration to a 4*s* orbital. In the UHF method the wave functions do not have to be pure spin states. By a simple algebraic projecting procedure we found the energies of the pure singlet states. The triplets were found to be almost pure spin states, within an error of 0.01%.

Table III tabulates the ground-state lattice configuration of NaF:Cu^+. The near-neighbor displacements are found to be less than 0.012 Å. The ground-state potential-energy curve for the nearest-neighbor distance is shown in Fig. 1. The equilibrium Cu^+-F^- distance for the ground state is found to be 2.31 Å or 4.36 a.u. From a parabolic fit of the energy curve, the harmonic force constant K of the vibrational breathing deformation of the defect cluster is found to be 10.0 eV bohr^{-2} or 5.7×10^5 g sec^{-2}. Correspondingly, the vibration energy quantum, $\hbar\omega$ or $\hbar(K/M^+)^{1/2}$, is deduced as 35.2 meV, where M^+ is 6 times the mass of a fluorine

TABLE III. Ground-state lattice configuration of NaF:Cu^+.

Ion		Displacement (Å)	Distance (Å)
Cu^+	(0,0,0)	0.0	0.0
F^-	(1,0,0)	0.0113	2.306
Na^+	(1,1,0)	0.0060	3.252
F^-	(1,1,1)	0.0003	3.975
Na^+	(2,0,0)	0.0026	4.593

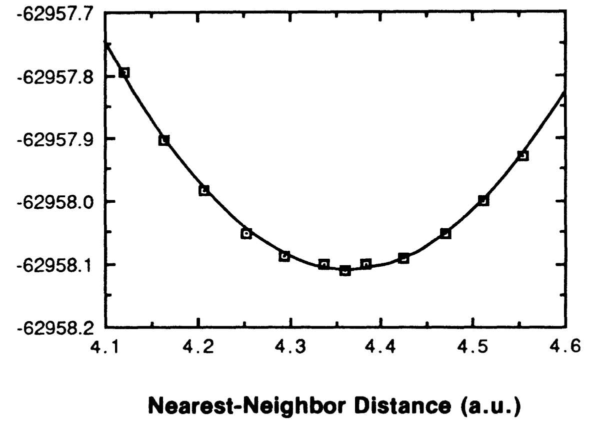

FIG. 1. Ground-state energy (eV) curve of NaF:Cu^+ vs nearest-neighbor distance (a.u.) (parabolic fit).

ion. This result is in very good agreement with the experimental value of 24.8 meV.[2]

In the crystal field of the NaF, the d orbital (-0.8207 a.u.) of the free Cu^+ ion is split into Γ_{12} and Γ'_{25} levels in the ground state and split into ${}^{1,3}\Gamma_{12}$ and ${}^{1,3}\Gamma'_{25}$ levels in the excited states with the spin-orbital splittings being omitted.

In Table IV the vertical excitation energies calculated without MBPT for NaF:Cu^+ at the calculated equilibrium nearest-neighbor separation are compared to the two-photon experimental results and to calculations by Winter *et al.*[19]

Ionization energies were calculated by taking off one of the d-type orbital electrons. The crystal-field splitting has been obtained by taking the difference between the ionization energies of the two d-type orbitals.

The calculated values of the $d \rightarrow s$ transition energy and the crystal-field splitting 10*Dq* are compared with the experimental and calculated values of Payne *et al.*[2] and Winter *et al.*[19] in Table V. By including the correlation correction we have obtained the $d \rightarrow s$ transition energy and the 10*Dq* as 4.02 and 0.31 eV, respectively, versus the experimental values of 4.20 and 0.35 eV, respectively.

TABLE IV. Comparison of the calculated energies for NaF:Cu^+ to experiment and to calculations by Winter *et al.*

	E (eV) (without MBPT)	E (eV) (expt.[a])	E (eV) (Winter *et al.*[b])
$d^{10}\ \Gamma_1$	0	0	0
$d^9s\ {}^3\Gamma_{12}$	3.03		2.95
$d^9s\ {}^3\Gamma'_{25}$	3.27	4.04	3.17
$d^9s\ {}^1\Gamma_{12}$	3.45	3.93	3.39
$d^9s\ {}^1\Gamma'_{25}$	3.70	4.43	3.65

[a] Reference 2.
[b] Reference 19.

TABLE V. Comparison of the excitation energy and the crystal-field splitting 10*Dq* with experiment (Ref. 2) and with the calculations of others.

	With MBPT	Without MBPT	Expt.	Payne[a]	Winter *et al.*[b]
$d \rightarrow s$ (eV)	4.02	3.60	4.20	3.60	3.50
10*Dq* (eV)	0.31	0.24	0.35	0.45	

[a] Reference 2.
[b] Reference 19.

IV. CONCLUSIONS

The present study represents the first calculation of an impurity spectrum in which lattice distortions and polarizations are computed self-consistently with the electronic structure, and the first application of ICECAP incorporating the correlation corrections. This study has demonstrated the ICECAP methodology. Even at the UHF level, without correlation correction, the calculated excitation energy 3.6 eV, and the 10*Dq*, 0.24 eV, are reasonable, and are comparable with the results of the DVM $X\alpha$ calculation by Payne *et al.*,[2] 3.6 and 4.5 eV, and the calculated value of 3.5 eV by Winter *et al.*[19] in terms of the finite cluster Hartree-Fock method. Including the correlation corrections, we have obtained 4.02 and 0.31 eV for the excitation energy and the 10*Dq*, respectively, which are in very good agreement with the corresponding experimental values of 4.2 and 0.35 eV. The significant improvement over the UHF level values demonstrates the need for including correlation correction in the ICECAP procedure.

The lattice distortions are 0.5% for the first-nearest neighbor, 0.2% for the second neighbor, and so on, as shown in Table IV. Consistent with the similar ion size of Na^+ and Cu^+ (0.95 and 0.96 Å, respectively), the Cu^+ impurity does not appreciably distort the lattice. However, the distortions have appreciable effect on the energy. The change in Coulomb energy between the defect and its nearest neighbors due to the distortions may be estimated as $\Delta = 6e^2\delta/r = 0.18$ eV for $\delta = 0.005$ and $r = 4.36$ a.u. Therefore the displacements of the six nearest neighbors may cause a change in the Coulomb energy that may be a significant fraction of the excitation energy of the 4.2 eV. In addition, the errors with respect to experiment (0.18 eV for the excitation energy, 0.04 eV for 10*Dq*) are comparable or small compared to this energy.

There are several more subtle features related to the ICECAP methodology. First the process that permits the separation of the system into a cluster and its environment is mathematically correct. This is a result of two circumstances. One is that the system is nonmetallic, and a fundamental description in terms of local rather than Bloch orbital is required. The other is that the localizing procedure provides a direct way of satisfying this requirement. The second feature is that the HADES part of ICECAP uses many experimental data to obtain relatively few parameters. The potentials based on them are then used extensively.

The Jahn-Teller splitting was found to be 0.15 eV for NaF:Cu$^+$ by Payne *et al.*[2] Winter *et al.*[19] calculated the spin-orbit splittings as 0.0025 eV for $^3\Gamma_{12}$ and about 0.01 eV for $^3\Gamma'_{25}$. However, we did not include the Jahn-Teller effect and the relativistic effect in the present study.

This work has been done on a Floating Point System FPS-164/MAX processor and a Digital Equipment Corporation VAX11/750 computer. On the FPS, with the compiling option 2, the CPU time for one cycle of the ICECAP energy-minimization routine including MBPT was 11.3 h for 80 basis functions (214 primitive Gaussians) and 183 UHF iterations. The computational cost of this rather precise method is not trivial. Implementation of the code on the supercomputers will undoubtedly enhance the applicability of the ICECAP methodology.

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