PHYSICAL REVIEW B VOLUME 38, NUMBER 14 15 NOVEMBER 1988-I

Cu^+ diffusion and interionic potentials for Cu^+ in alkali halides

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(Received 21 April 1988)

Short-range interionic potentials for the substitutional Cu^+ ion in alkali fluorides and chlorides are derived using a methodology that provides self-consistent electronic-structure treatment of a molecular cluster of ions that includes the impurity, embedded in a shell model lattice. The derived potentials are used to calculate the activation energy for Cu^+ diffusion by the cation vacancy mechanism in these materials. For the only case where an experimental value is available, namely, KCl:Cu^+, satisfactory agreement is found.

INTRODUCTION

The electronic structure and optical properties of substitutional Cu^+ in NaF have been studied in great detail by ourselves[1] using a methodology contained in our program ICECAP.[2] The ICECAP program treats the impurity copper and its vicinity as a quantum-mechanical cluster embedded in the shell-model lattice. The electrons in the cluster are treated in the unrestricted Hartree-Fock self-consistent-field approximation (UHF-SCF) corrected for correlation by the use of many-body perturbation theory.[3] The electronic energy levels and the excitation energies of Cu^+ in NaF have been calculated.[1] The results provide good agreement with the corresponding experimental values. We now extend the investigation to the transport properties of Cu^+, calculating the activation energy for its diffusion in NaF and other alkali halides. First, we derive the short-range interionic potential between the Cu^+ ion and its nearest neighbors in the host lattice using ICECAP. The derived potentials are then used to evaluate the activation energy for Cu^+ diffusion in alkali halides.

COMPUTATIONAL METHOD

In the present work we use the program package HADES,[4] which has proven to be successful in simulating the atomic transport processes of intrinsic and extrinsic defects in alkali halides.[5] Briefly, HADES divides the lattice into two regions: an inner region immediately surrounding the defect, where the lattice configuration is evaluated explicitly using pairwise potentials which represent the ionic interactions, and an outer region which is treated by the Mott-Littleton approximation using information on macroscopic response functions, namely the elastic and dielectric constants of the lattice. HADES uses the shell model, originally proposed by Dick and Overhauser,[6] to simulate the ionic polarization in the lattice. A wide variety of defect calculations based on HADES in ionic and semi-ionic materials[7] has led to the conclusion that the accuracy of the calculated defect energies depends mainly on the quality of pairwise potentials used to model the lattice.

In alkali halides, Catlow and his co-workers[8] have obtained semiempirical pairwise potentials for the host-lattice ions representing the (non-Coulombic) short-range interaction by Buckingham-type potentials. They have derived short-range anion-anion interaction from free-ion Hartree-Fock potential curves and then fitted both cation-cation and cation-anion interactions to crystal data such as lattice spacing, cohesive energy, and elastic constants. Their approach, however, relies heavily on the availability of crystal data. Alternatively, Mackrodt and Stewart[9] have used the (nonempirical) electron-gas method to derive pairwise potentials. They have concluded that careful choice of basis sets for interacting ions and the correct representation of the crystalline modeling field are essential for obtaining reliable interionic potentials. In the present work we have used the semiempirical potential set referred to as set II by Catlow *et al.*[8] for the host-lattice ions in the alkali halides.

The calculation of pairwise potentials interacting between impurity ions and host crystal ions has proved to be a difficult task. In earlier attempts, either an arbitrary method was used to extract the potentials from the defect (impurity) crystal[10] or the electron-gas method was employed for deriving the potentials.[11]

Spectroscopic measurement[12] shows that copper in NaF occupies the on-center position as Cu^+ substituting in the lattice for Na^+ ion. The coordination of Cu^+ is therefore octahedral. Although two fluorides of copper exist,[13] neither has the NaCl-type structure. Cuprous fluoride (CuF) has the zinc-blende structure, where Cu^+ has fourfold coordination. Cupric fluoride (CuF_2) is monoclinic. Thus neither of these provides a suitable basis from which to take shell-model parameters for substitutional Cu^+ in NaF, but particularly not CuF_2, where Cu has charge state (+ 2). Furthermore, no shell-model fit has so far been made to the properties of CuF.

Because Cu^+ is a tightly bound cation, both its polarizability and its second-neighbor interactions with Na^+ ions in NaF may be negligible. This is what has been observed in CuCl, with the tetrahedrally coordinated zinc-blende structure, by Prevot *et al.*[14] They have analyzed the phonon spectrum of CuCl within the shell-model formalism and have observed that second-neighbor interactions do not play a significant role in the fitting process. They have also obtained a very low value of polarizability for Cu^+ in CuCl. Therefore, we may reasonably assume that Cu^+ in NaF is unpolarizable, with negligible second-neighbor (Cu^+—Na^+) interactions.

We now use the ICECAP-HADES methodology to derive the first-neighbor (Cu^+—F^-) pairwise interaction. In ICECAP, the NaF:Cu^+ system is simulated by a $Cu^+(F^-)_6$ Hartree-Fock cluster embedded in the shell-model NaF lattice. We want a $Cu^+(F^-)_6$ shell-model cluster whose energy dependence on configuration will simulate the corresponding Hartree-Fock cluster, when both are embedded in identical NaF shell-model crystals.

Let us consider the symmetrical (O_h) distortion of the $Cu^+(F^-)_6$ cluster and let d be the nearest-neighbor (Cu^+—F^-) distance in this cluster. Also, let $E(d)$ be the total crystal energy with the Hartree-Fock cluster. For the shell-model cluster, let $B(A,\rho,C;d)$ be the nearest-neighbor (Cu^+—F^-) short-range potential,

$$B = A\exp(-d/\rho)-(C/d^6)\ . \tag{1}$$

This is a Buckingham potential of the same form that we use for the NaF crystal. Then we require

$$E(d)=\varepsilon^{(0)}(d)+6B(A,\rho,C;d)+k\ . \tag{2}$$

In Eq. (2), $\varepsilon^{(0)}(d)$ is the shell-model energy obtained by HADES when the cluster has configuration d, with Cu^+—F^- short-range potentials omitted, $6B$ introduces those potentials, and k is an additive constant to account for the fact that $E(d)$ includes internal electronic energy of the cluster ions. In practice, we renormalize $E(d)$ so that it is comparable to $\varepsilon^{(0)}(d)$. Now if we know $E(d)$ and $\varepsilon^{(0)}(d)$ for four values of d, we can solve Eq. (2) for A, ρ, C, and k. A library routine has been used to evaluate the roots of a system of equations,

$$f_i(x_1,x_2,x_3,x_4)=0,\quad i=1,2,3,4 \tag{3}$$

by minimizing and reporting

$$S=\sum_i |f_i|^2\ . \tag{4}$$

Since we want energies accurate to about (0.05 eV), we require $S \lesssim 4(0.05)^2=10^{-2}$ eV. In Eq. (3), $x_1=A$, $x_2=\rho$, $x_3=C$, $x_4=k$, and

$$f_i=[\varepsilon^{(0)}(d_i)-E(d_i)]+6B(A,\rho,C;d_i)+k\ . \tag{5}$$

Thus, the derivation of the (Cu^+—F^-) short-range potential requires (i) that we evaluate the ICECAP energy for a $Cu^+(F^-)_6$ cluster with four values of d; (ii) do the same with HADES, omitting (Cu^+—F^-) short-range interaction, and (iii) solve Eq. (3) with Eqs. (4) and (5).

In ICECAP-HADES calculations, we have taken $d_1=0.94a$, $d_2=0.98a$, $d_3=1.02a$, and $d_4=1.06a$, where a is the NaF perfect-lattice nearest-neighbor spacing. This allows for up to 6% compression and dilatation of the cluster. All electrons in the Hartree-Fock cluster are explicitly included in the ICECAP calculation. Gaussian basis sets associated with Cu^+ and F^- ions are taken from Meng[1] and Huzinaga's compilation,[15] respectively. The optimized basis set for Cu^+ is the (533/53/5) contraction whereas that for F^- is the (433/43) contraction. It is to be noted here that the nearest-neighbor spacing (2.295 Å) used in these calculations for NaF is slightly smaller than the experimental value of 2.32 Å.

RESULTS AND DISCUSSION

The derived (Cu^+—F^-) short-range potential is given in Table I. We now evaluate the equilibrium configuration of the NaF:Cu^+ system using HADES. Here, the Cu^+ ion is constrained to sit on the Na^+ lattice site with fully symmetric relaxation of neighboring ions. The (Cu^+—F^-) distance in the equilibrium configuration comes out to be $0.99a$ comparable to the value ($1.005a$) that was obtained in the Hartree-Fock (ICECAP) calculation. Furthermore, the assumption that the Hartree-Fock and the shell-model descriptions of short-range (F^-—F^-) interaction are equivalent, on which Eq. (2) is based, is supported by Vail *et al.*[16] In the latter reference, Table I, for the cluster NaF_6, the energy discrepancy for $d=0.05a$ is 0.06 eV. Thus the quantum and classical representations of the (Cu^+—F^-) short-range interaction are compatible in the present study.

The derived (Cu^+—F^-) potentials are now used in a HADES calculation to estimate the thermal activation energy for diffusion of Cu^+ in NaF by the vacancy mechanism. This is simply the difference of HADES energies $\Delta E=(E_A-E_0)$ for the defect configurations shown in Fig. 1. Assuming the transferability of (Cu^+—F^-) potentials to the other alkali fluorides, we have also calculated the Cu^+ activation energy in LiF, KF, and RbF crystals. The results are given in Table II. The trend appears to be associated with the nearest-neighbor spacing of alkali fluorides; the activation energy is smaller for a fixed host-anion as the host-cation becomes larger, which seem reasonable. The relaxed position coordinates (x,y) of a Cu^+ ion and of a halide ion adjacent to the Cu^+ ac-

TABLE I. Parameters of the Buckingham short-range interionic potential for Cu^+ in alkali halides,

$$V_{ij}=A_{ij}\exp(-r/\rho_{ij})-C_{ij}r^{-6}\ .$$

	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV Å^6)
Cu^+—F^-	3769.4	0.2570	71.7
Cu^+—Cl^-	7545.1	0.2977	411.3

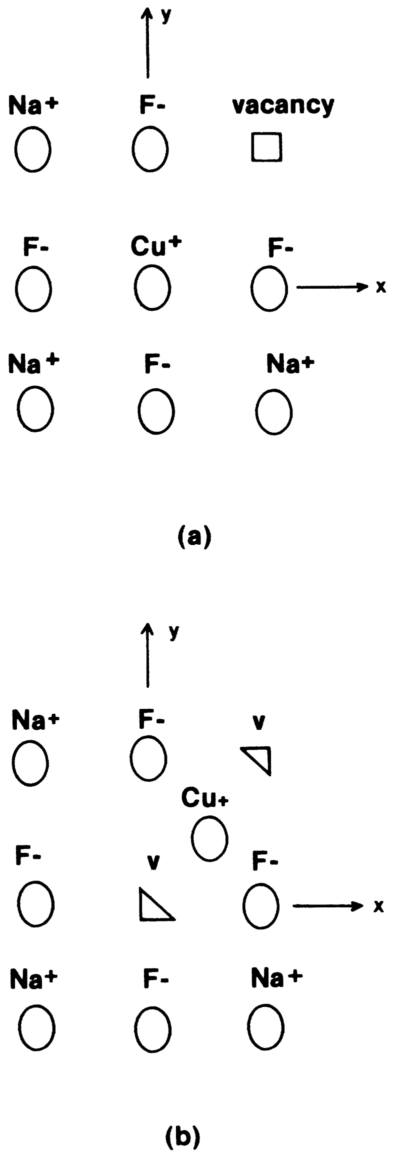

FIG. 1. Thermal activation of Cu^+ diffusion by the vacancy mechanism In NaF. (a) Initial configuration. (b) Activated configuration.

TABLE III. Relaxed position coordinates (x,y) in units of perfect lattice spacing (a) of a Cu^+ ion, and of a halide ion adjacent to the Cu^+ activated position, for initial and activated configurations [Figs. 1(a) and 1(b), respectively] for the vacancy diffusion mechanism in NaF and KCl.

		Initial Configuration	Activated Configuration
NaF	Cu^+	$(0.01,0.01)$	$(0.50,0.50)$
	F^-	$(0.98,-0.09)$	$(1.12,-0.13)$
KCl	Cu^+	$(0.01,0.01)$	$(0.50,0.50)$
	Cl^-	$(0.88,-0.06)$	$(1.08,-0.08)$

tivated position for initial and activated configurations are given in Table III.

No experimental study on Cu^+ diffusion in alkali halides has so far been reported except that in KCl and KBr. Henke *et al.*[17] have obtained activation energies of 1.1 and 1.0 eV for Cu^+ diffusion in KCl and KBr, respectively, attributing the process to the vacancy mechanism. We have therefore calculated the activation energy for the Cu^+ diffusion in KCl and have compared with the experimental result. To do so, we have derived the $(Cu^+—Cl^-)$ short-range potential using the same procedure as described above for $(Cu^+—F^-)$. Table I includes the derived $(Cu^+—Cl^-)$ potential. The calculated activation energy of Cu^+ diffusion by the vacancy mechanism comes out to be 1.19 eV in KCl, showing good agreement with the experimental result of 1.1 eV.[17]

We have applied the $(Cu^+—Cl^-)$ potential to the other rocksalt-structure chlorides, LiCl, NaCl, and RbCl. The calculated Cu^+ activation energies for the vacancy mechanism are included in Table II. Also indicated in Table II is information about the displacements of near-neighbor ions by a substitutional Cu^+ [without the associated vacancy of Fig. 1(a)], as calculated with our derived potentials from Table I.

We note that the short-range potentials obtained here from a simple, symmetrical configuration are applied to the lower-symmetry activated configuration (Fig. 1). In general, the extension of short-range potentials from high to low symmetry problems is questionable, requiring full

TABLE II. Calculated activation energies ΔE for the substitutional Cu^+ diffusion by vacancy mechanism in alkali fluorides and chlorides. Also perfect lattice nearest-neighbor spacing a, and equilibrium positions d of nearest (100), second (110), and third (111) neighbors of substitutional Cu^+ without an associated vacancy, as fractions of their perfect lattice distances from a central cation site.

Crystal	ΔE (eV)	a (Å)	$d(100)$	$d(110)$	$d(111)$
LiF	1.17	1.996	1.06	1.01	0.995
NaF	1.05	2.295	0.987	0.997	0.999
KF	0.83	2.648	0.907	0.984	1.000
RbF	0.76	2.789	0.871	0.981	1.001
LiCl	1.31	2.539	1.033	1.006	0.994
NaCl	1.27	2.789	1.003	0.999	0.997
KCl	1.19	3.116	0.896	0.984	0.999
RbCl	1.10	3.259	0.862	0.979	1.000

Hartree-Fock treatment of Fig. 1, for example. Nevertheless, such calculations have been done successfully for both intrinsic and extrinsic defects in ionic and semi-ionic materials.[7,10,11]

Furthermore, the results calculated here for Cu^+ diffusion by the vacancy mechanism are based on neglect of second-neighbor impurity-host short-range interaction, and assume transferability of nearest-neighbor (Cu^+) host-anion short-range potential from a given alkali halide to others with different alkali species. These issues should be investigated when adequate comparison with experimental results becomes available.

In summary, we have demonstrated that interionic potentials derived from a Hartree-Fock cluster produce encouraging results. In particular, the satisfactory agreement between the calculated and observed activation energy of Cu^+ diffusion in KCl is an indication of reliability for these derived potentials. The method therefore makes possible the derivation of (impurity-host) interionic potentials which cannot be obtained from bulk crystal properties.

ACKNOWLEDGMENTS

This work was in part supported by U. S. Department of Energy under Grant No. DE-FG02-85-ER45224 and by the Natural Science and Engineering Research Council, Canada.

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