First-principles calculations of the vibrational properties of *H* centers in KCl crystals

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The atomic and electronic structure of the radiation-induced interstitial halide atoms in KCl crystals (called *H* centers) is calculated using 16-atom supercells and the first-principles full-potential linear muffin-tin orbital method. The vibrational properties of the *H* centers are studied for the two orientations of the molecular axis of the *H* centers known to exist in alkali halide crystals — along the (110) and (111) axis. Only in the former case (which is known to be energetically more favorable in KCl), the local vibrational frequency is close to that experimentally observed by means of Raman spectroscopy. A strong coupling is found between the stretching molecular mode of the *H* center and the breathing motion of its six nearest K^+ cations. This is predicted to result in another local mode around 257 cm^{-1}.

The primary radiation Frenkel defects in alkali halides, *MX*, are known to be *F* (an electron trapped by a halogen vacancy) and *H* centers.[1] The latter is an interstitial halogen atom, X_i^0, forming a chemical bond with the nearest regular halogen ion, X^-. This results in the X_2^- quasimolecule occupying a single site in the anion sublattice. Although the optical and paramagnetic properties of the *H* centers could be well described in terms of the molecular properties,[2,3] the crystalline environment can affect their vibrational properties considerably. Theoretical studies are stimulated by careful resonant Raman-spectroscopic experiments[4] done for a number of alkali halide crystals.

Only few quantum mechanical studies of the *H* centers have been done so far,[5–7] with a single theoretical attempt to calculate the *H* center stretching frequency.[8] Careful studies of the vibrational properties of the diatomic molecular centers are important for understanding the structure of the self-trapped excitons in alkali halide crystals: whether their hole core is a slightly off-center X_2^- quasimolecule occupying two anion sites (the so-called V_K center, or self-trapped hole) or it is closer to the *H* center.[1] The calculations of the *H* center electronic structure[8] considered small quantum clusters embedded in an infinite crystal. The approximate treatment of the latter may affect the calculated properties of the defect. In the present paper we use a *periodic*, *supercell* model of the *H* center combined with a first-principles method for the calculation of its atomic and electronic structure.

The full-potential linear muffin tin orbital (FP LMTO) method based on the local density approximation (LDA) for the treatment of exchange and correlation effects is described in detail in Ref. 9. In the present calculations we included almost touching muffin tin (MT) spheres of approximately equal size on K^+ and Cl^- as well as additional empty spheres necessary to improve the charge density fit. Electronic eigenstates were expanded in a basis set of 17 MT orbitals per atom (3*s*, 3*p*, and 1*d* set). The K^+ 3*p* semicore states were included as valence electrons.

The 16-atom supercell is a primitive fcc unit cell which is extended twice along all three translation vectors. The optimized lattice constant is found to be $a_0 = 6.103$ Å which is 2.3% smaller than the experimental value of 6.246 Å measured[10] close to 0 K — see Fig. 1(a). The calculated bulk modulus is $B = 29.1$ GPa, considerably larger than the experimental value of 20.8 GPa deduced from data in Ref. 10. These findings are typical for the LDA formalism used here. Thus, in similar calculations for NaCl we have found $a_0 = 5.483$ Å and $B = 31.3$ GPa, to be compared with the relevant experimental values of 5.597 Å and 27.8 GPa, respectively. The LDA approximation obviously tends to underestimate the lattice parameters and to overestimate the bulk modulii of ionic solids. However, the discrepancy is reduced if we incorporate into the theory the effect of zero-point motion. Following Ref. 11, one can express the zero-point energy through the Debye temperature, Θ_D, $E_0 \approx 1/2 \hbar \omega_D = 1/2 k_B \Theta_D$. The Debye frequency may be taken proportional to the square root of the bulk modulus[11]

$$E_0(V) = E_0(V_0)(B/B_0)^{1/2}, \qquad (1)$$

where V_0 is the equilibrium volume. Thus the zero-point motion increases the pressure by

$$P_0 = -\frac{\partial E_0}{\partial V} = \frac{E_0 B_0'}{2V_0}, \qquad (2)$$

where $B_0' = \partial B_0 / \partial P$. The corresponding change, ΔV, in equilibrium volume is
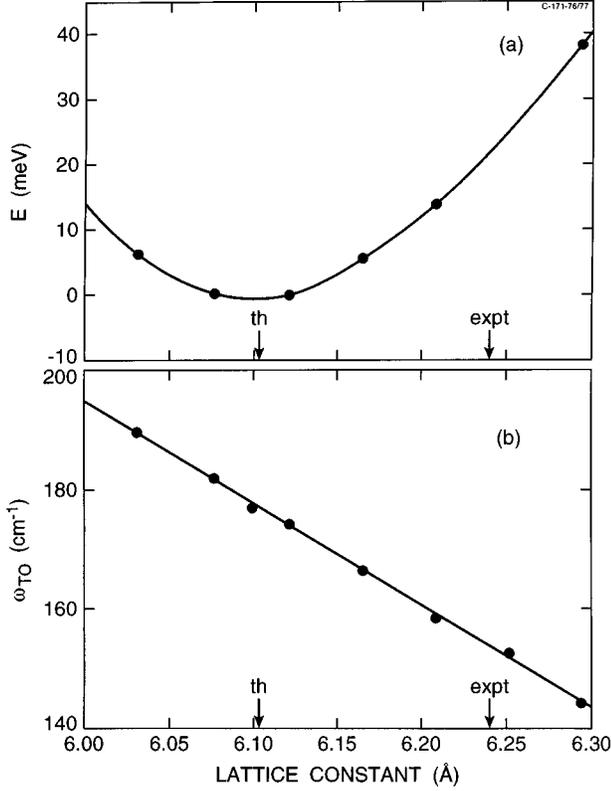
$$\Delta V = \frac{P_0}{B_0} V_0. \qquad (3)$$

FIG. 1. (a) The total energy as a function of the lattice constant a; a_0 is the experimental value of 6.24 Å. (b) The TO phonon frequency vs a; arrows indicate the theoretical and experimental lattice parameters.

The bulk modulus at the corrected equilibrium volume is $B_0 + \Delta B$, where

$$\frac{\Delta B}{B_0} = -B_0' \frac{\Delta V}{V_0}. \qquad (4)$$

Using now the calculated value of $B_0' = 5$ and the experimental value of $\Theta_D = 231$ K, one gets $\Delta V/V_0 = 1.5\%$ and $\Delta B/B_0 = -7.5\%$. The corrected lattice parameter and the bulk modulus become now $a_0' = 6.133$ Å and $B = 26.9$ GPa. This is in better agreement with the experimental data quoted above.

It should be stressed here that the alternative first-principles approach to the electronic/atomic structure calculations — the Hartree-Fock method — neglects the electron correlation effects and thus gives considerable *overestimate* of the lattice constant and *underestimate* of the bulk modulus, in contrast to what we have in the LDA calculations. In particular, the recently reported Hartree-Fock calculations[12] for NaCl yield $a_0 = 5.80$ Å and $B = 22.8$ GPa, which gives relative differences from the experimental values 3.5% and -14.3%, respectively. This discrepancy is of the same order of magnitude as obtained in the present LDA study (-2.1% and 17.7%, respectively, before zero-motion corrections).

The calculated frequency of TO phonons at the Γ point of the Brillouin zone using the theoretical lattice constant is

TABLE I. Equilibrium atomic configurations of the H center in KCl oriented along the (110) and (111) axis (in units of $a/2$, a being the calculated equilibrium lattice constant). Coordinates of only one atom from a set of equivalent atoms are given. The numbering of the atoms is shown in Fig. 3(a).

	FP LMTO			ICECAP (Ref. 7)		
(110)						
Cl_1	0.297	0.297	0.0	0.289	0.289	0.0
Cl_2	1.0	1.0	0.0	1.02	1.02	0.0
K_1	1.104	-0.042	0.0	1.13	-0.07	0.0
K_2	0.0	0.0	0.90	0.0	0.0	0.96
K_3	1.0	1.0	0.987	1.0	1.0	1.0
(111)						
Cl_1	0.237	0.237	0.237			
$K_{1,2}$	1.06	-0.019	-0.019			
K_3	1.0	1.0	1.0			

177 cm^{-1} which is 20% higher than the experimental value of 146 cm^{-1}. Employing the Lyddane-Sachs-Teller relation, $\omega_{LO} = \sqrt{\epsilon_0/\epsilon_\infty}\,\omega_{TO}$,[13] we obtain the theoretical/experimental frequencies of the LO phonons as 256 cm^{-1} and 211 cm^{-1}, respectively. As is seen from Fig. 1(b) this discrepancy arises entirely from the theoretical lattice constant a_0 being too small; for the experimental a_0 the calculated TO phonon frequency of 155 cm^{-1} turns out to be much closer to the experimental value.

From the electron spin resonance (ESR) measurements it is known that the orientation of the H molecular axis varies from one alkali halide crystal to another;[1] in KCl it lies along the (110) axis whereas in NaCl — along the (111) axis. In this work we examine both orientations. For the (110) case the total energy has been calculated as a function of five basic displacements of ions: the distance between the two Cl atoms constituting the H center, and three kinds of cation displacements: x, y displacements of four nearest-neighbor (NN) K$^+$ lying in the same plane as the X_2^- molecule, displacements along the z axis perpendicular to this plane of the two nearest K$^+$ ions, and similar z displacements of six NNN K$^+$ ions in the corners of the cube. Note that the two NN Cl ions lying along the (110) axis cannot be relaxed due to the symmetry of the supercell geometry. For the (111) orientation all six NN K$^+$ cations turn out to be equivalent.

In the vicinity of the equilibrium geometry the total energy can be fitted to the second-order form:

$$U(\vec{x}) = E_0 + \vec{E_1} \cdot \vec{x} + \frac{1}{2}\vec{x}^\dagger A \vec{x}, \qquad (5)$$

where E_0 and $\vec{E_1}$ are constants, $\vec{x}$ is a vector whose five components x_i are the above-mentioned atomic displacements, and $A = \|A_{ij}\|$ the dynamical matrix. It is convenient to introduce in the equation of motion the reduced coordinates, $y_i = \sqrt{m_i}x_i$, in which it reads
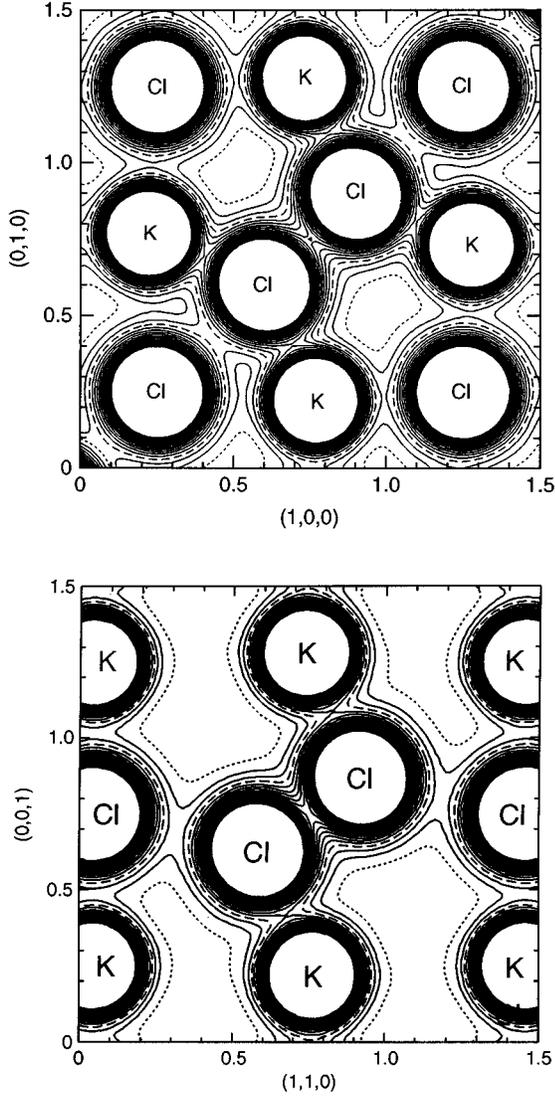
$$\ddot{y}_i = \sum_j \alpha_{ij}y_j. \qquad (6)$$

FIG. 2. The electronic density distribution in the H center for its two orientations — along the (110) and (111) axis. The increment is 0.005 e (a.u.)$^{-3}$, the dotted and dashed line show densities of 0.005 and 0.02 e (a.u.)$^{-3}$, respectively.

The reduced dynamical matrix $\alpha_{ij} = A_{ij}/\sqrt{m_i m_j}$ defines directly the local frequencies ω_i sought for, which are roots of the determinant

$$\det|\alpha_{ij} - \omega^2 \delta_{ij}| = 0. \qquad (7)$$

The off-diagonal elements of the dynamical matrix, α_{ij}, $i \neq j$ characterize the coupling of different modes. Putting some of these elements to zero allows us to study the individual vibrational modes and their coupling effects.

Table I shows the optimized positions of atoms constituting the H center and its surrounding. For the (110) case they are in a good agreement with cluster Hartree-Fock calculations (ICECAP computer code[7]). The X_2^- bond lengths are $R = 2.55$ Å and 2.50 Å for the (110) and (111) orientations respectively, both shorter than the equilibrium distance in the free X_2^- molecule (2.76 Å). The total energy is lower for the

TABLE II. The calculated vibrational frequencies (in cm^{-1}) of the H center for the two possible orientations of its axis and the effect of the coupling of different vibrational modes for the (110) case. Figures in brackets correspond to calculations using the experimental lattice constant.

Coupling type	X_2^- molecule stretching	Cation breathing
(110) orientation		
no coupling	268	270
	(250)	(241)
Coupling via motion		
of 4 NN in-plane K$^+$	306	225
	(276)	(211)
Plus motion of 2 NN		
K$^+$ ions along z axis	306	235
Plus motion of 6 NNN		
K$^+$ ions	307	235
Expt. (Ref. 4)	329	
ICECAP (Ref. 8)	314	
(111) orientation		
complete coupling	273	224

(111) orientation which contradicts the experimental preference in favor of the (110) orientation. This could result from a smallness of the supercell used in which NN Cl ions are fixed in their sites by symmetry constraints. However we assume that solution of this problem goes beyond the accuracy of first-principles calculations of defects in ionic solids like the H center characterized by a strong, long-range relaxation and using small supercells like here. From a comparison of the total energies obtained using the experimental and calculated lattice constants, as well as our H center geometry and that from Ref. 7 we estimate the uncertainty in the total energy calculation to be $\approx$ 0.3 eV, an order of magnitude larger than the experimentally estimated energy difference between these two orientations. It should be mentioned that the previous calculations[6,7] also failed to reproduce the (110) orientation as energetically more favorable.

Figure 2 shows the electronic density distribution for the H centers in two orientations. Unlike the (111) orientation, in the (110) case there is certain electronic charge concentration between the dumbbell atoms and the two nearest Cl ions — in agreement with the experimental data.[1] The (111) H center has a larger electron density concentration between the two atoms, probably, due to a shorter equilibrium distance between them.

The calculated vibrational frequencies are given in Table II. We started with the full dynamical matrix, as descibed above [Eq. (3)], and then simulated the effect of different mode decoupling, one mode at a time. In the (110) case the highest local frequency of 307 cm^{-1} is much closer to the Raman experimental value of 329 cm^{-1} than that for the
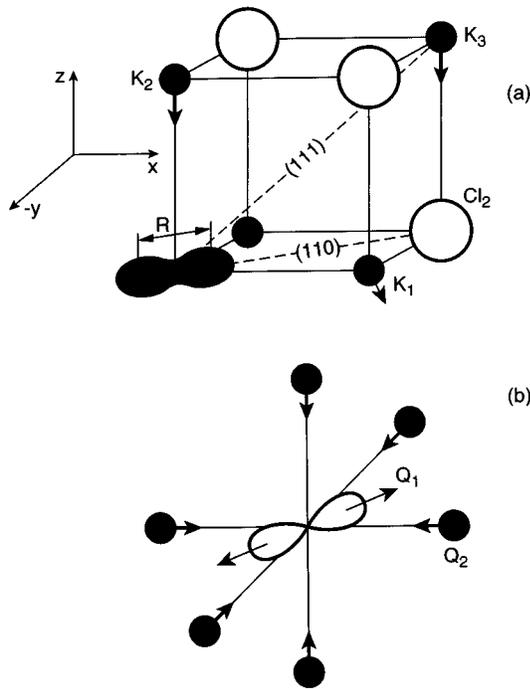
FIG. 3. (a) Equilibrium (on-site) atomic configurations of the H center. (b) The two local modes of high-frequency vibrations are the stretching of the quasimolecule (Q_1) and the breathing of the six NN cations (Q_2).

NN K^+ cations lying at the same plane as X_2^- [Fig. 3(a)]. In the (110) case the individual (decoupled) stretching and breathing modes have very close frequencies — 268 cm^{-1} and 270 cm^{-1}. At the next stage we allow them to be coupled via motion of the 4 NN in-plane K^+ cations which results in the 81 cm^{-1} gap between these two basic modes. Further incorporation of the motion of the two NN K^+ cations lying along the z axis changes the breathing mode only (by 10 cm^{-1}). Lastly, motion of six NNN K^+ ions does not affect any of the two vibrational modes. Lastly, in the brackets of Table II we give also the vibrational frequencies calculated for the *experimental* lattice constant. They are significantly lower than those calculated for the theoretical lattice constant.

As a result of a strong coupling of the stretching and breathing modes we expect *two* Raman frequencies to exist in KCl. Along with the observed frequency at 329 cm^{-1}, another frequency is estimated in our calculations to lie 72 cm^{-1} lower, i.e., around 257 cm^{-1}. Note that paired Raman spectra have been indeed observed in KBr and NaBr.[4]

For the (111) orientation the stretching-breathing coupling is much weaker, the splitting is smaller (40 cm^{-1}), and the stretching mode of the H center falls down to 273 cm^{-1}, that is closer to the continuum phonon spectrum.

In conclusion, we predicted the additional Raman vibrational mode of the H center in KCl and demonstrated that the vibrational properties of diatomic molecules are much more sensitive to their orientation than the total energy.

(111) case. Our calculations support the idea[4] of a strong coupling of the stretching X_2^- molecular mode and the breathing mode of NN K^+ ions as shown in Fig. 3(b). Due to the presence of an anisotropic (110) H center two K^+ cations lying along the z axis are no longer equivalent to four other

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