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Cluster–Bethe-lattice treatment for the U_2 center in alkali halides*

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A cluster–Bethe-lattice calculation for the electronic density of states of a U_2 center in the rocksalt structure is presented for a simple one-orbital Hamiltonian. The parameters involved in the Hamiltonian are given values based on qualitative arguments for Na, K, Rb chlorides and bromides and the proton contact term is calculated for these sets of parameters, in fair agreement with experimental data.

I. INTRODUCTION

Recently, a very simple theoretical approach—the cluster–Bethe-lattice method—was proposed for the study of several properties of solids. It has been successfully applied to a variety of problems, such as the electronic density of states in crystalline and amorphous solids,[1,2] alloys,[3,4] and spin-wave spectra in dilute ferromagnets.[5]

This approach is, in the choice of basis functions, equivalent to a linear-combination-of-atomic-orbitals (LCAO) method, and has the advantage of treating not only a limited number of atoms, but the whole crystal by means of a boundary condition which consists of attaching a Bethe lattice to each of the atoms in the frontier of a chosen cluster. A Bethe lattice (or Cayley tree) is a topological construction: an infinitely connected system of atoms of fixed coordination number, such that every atom is equivalent and there are no rings of bonds in the system.

Such approach is very convenient to study defects in solids, since in a simple analytic manner, it is possible to treat exactly a cluster containing a limited number of atoms surrounding the defect, and due to the chosen boundary condition, the approximate bulk states are obtained simultaneously.

This method was recently used to study α centers (vacancy states) in alkali halides,[6] but no experimental comparison was attempted. In the present work, another type of defect in alkali halides, the U_2 center (interstitial hydrogen atom), is treated by the same method.

The U_2 center is simple enough so that a lot of theoretical work has been done to describe its electronic structure.[7-13] The usual approach to describe the wave function is based on a one-electron formalism—basically using the Heitler-London method,[7-9] or a LCAO–molecular-orbital approach,[8-13] in a spin-restricted scheme. The multiple-scattering method in the $X\alpha$ approximation has been recently used to study the electronic structure of the interstitial hydrogen atom in KCl,[14] and in alkaline-earth fluorides.[15] These methods are cluster-type, and are not able to account for band states.[16]

As discussed above, the cluster–Bethe-lattice approach is capable to represent band states as well as localized-impurity states. In the choice of the Hamiltonian, we restrict our basis to s-like orbitals localized at anion and cation sites, and introduce a hydrogen $1s$ orbital. Of course this is a limitation of the model Hamiltonian, and we shall not attempt to use it for a detailed description of the alkali-halide electronic structure.

In Sec. II we define the Hamiltonian for the U_2 center in alkali halides, and give a brief review of the theory. The results for the local density of states are in Sec. III. In Sec. IV we present qualitative arguments for the choice of the parameters introduced in the Hamiltonian, and using these particular values, we are able to account for the experimentally observed proton contact interaction in several alkali halides.

II. THEORY

We describe the perfect heteropolar crystal by the following Hamiltonian:

$$H_0 = \pm\Lambda \sum_i |i\rangle\langle i| + V \sum_{\substack{i\neq j \\ \text{nearest} \\ \text{neighbors}}} |i\rangle\langle j| , \tag{1}$$

where $|i\rangle$ is an s-like orbital localized on site i; V is the hopping integral between nearest neighbors. The origin of energies is taken in such a way that the diagonal element of H_0 is $+\Lambda$ or $-\Lambda$ according to whether i is a cation or an anion site. The defect perturbs the crystal, so that the model Hamiltonian for the system can be taken as

$$H = H_0 + H' , \tag{2}$$

$$H' = \Lambda_0 |0\rangle\langle 0| + V^{+} \sum_{\alpha=1}^{4} (|0\rangle\langle i_\alpha| + |i_\alpha\rangle\langle 0|) + V^{-} \sum_{\beta=1}^{4} (|0\rangle\langle i_\beta| + |i_\beta\rangle\langle 0|) , \tag{3}$$

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where $|0\rangle$ is the interstitial hydrogen 1*s* orbital, the sum in α (β) is taken over the four cation (anion) sites nearest to the impurity, V^+ (V^-) is the hopping integral between the hydrogen orbital and one of its neighboring cation (anion) orbitals. Since the U_2 center is a neutral defect, and according to the choice for the origin of energies discussed above, it is reasonable to assume $\Lambda_0 = 0$. Our cluster consists of the interstitial hydrogen atom together with its eight nearest neighbors. Each cation (anion) in the cluster has coordination number 7: three links are with anions (cations) in the cluster, one is with the impurity and the three heteropolar Bethe lattices attached to it simulate the rest of the crystal (see Fig. 1).

The local density of states (LDOS) at the impurity site is obtained from the diagonal matrix element of the Green's function $\langle 0|G|0\rangle$, which can be evaluated with the use of Dyson's equation, as extensively discussed in previous papers[1,2,6]:

$$E\langle i|G|j\rangle = \delta_{ij} + \sum_k \langle i|H|k\rangle\langle k|G|j\rangle . \tag{4}$$

Two types of contributions to the LDOS are obtained: states in the continuum are given by

$$\eta_0(E) = -(1/\pi)\,\mathrm{Im}(\langle 0|G|0\rangle) \tag{5}$$

and localized or δ-function states exist at the poles of $\langle 0|G|0\rangle$. The weight of a pole at energy $E = P$ at any particular site i, is[3]

$$W_i(P) = \mathrm{res}_{E=P}(\langle i|G|i\rangle) . \tag{6}$$

Expressions (5) and (6) are normalized so that the integrated density of states at each site is 1.

For the chosen cluster, the diagonal matrix element $\langle 0|G|0\rangle$ can be obtained from the following set of linear equations:

$$\begin{aligned}&(E-\Lambda_0)\langle 0|G|0\rangle = 1 + 4V^+\langle +|G|0\rangle + 4V^-\langle -|G|0\rangle ,\\ &(E \mp \Lambda - 3\phi^\pm)\langle \pm|G|0\rangle = V^\pm\langle 0|G|0\rangle + 3V\langle \mp|G|0\rangle .\end{aligned} \tag{7}$$

The solution of (7) for $\langle 0|G|0\rangle$ is

$$\langle 0|G|0\rangle = \frac{E^+E^- - 9V^2}{E_0(E^+E^- - 9V^2) - 4[(V^+)^2E^- + (V^-)^2E^+ + 6VV^+V^-]} , \tag{8}$$

where

$$\begin{aligned}E^+ &= E - \Lambda - 3\phi^+ ,\\ E^- &= E + \Lambda - 3\phi^- ,\\ E_0 &= E - \Lambda_0 ,\end{aligned} \tag{9}$$

and $|+\rangle$ ($|-\rangle$) represent the orbital at a cation (anion) site. The field operators ϕ^+ (ϕ^-) depend only on the properties of the Bethe lattice and simulate mathematically the effect of an heteropolar Bethe lattice acting along one link on a positive (negative) ion. In the case of the alkali halides, they are[2]

$$\begin{aligned}\phi^+(E) &= \frac{1}{10}\left(E_2 \pm \frac{[E_1E_2(E_1E_2 - 20V^2)]^{1/2}}{E_1}\right),\\ \phi^-(E) &= \frac{1}{10}\left(E_1 \pm \frac{[E_1E_2(E_1E_2 - 20V^2)]^{1/2}}{E^2}\right),\end{aligned} \tag{10}$$

where $E_1 = E + \Lambda$ and $E_2 = E - \Lambda$.

The choice of the sign of the square root is discussed in Refs. 1, 2, and 6. It is easily shown that $\phi^+(E)$ and $\phi^-(E)$ must have the same sign. For the energy regions where $\eta_0(E)$ is a continuum, the plus sign is chosen when $E < -\Lambda$ and the minus sign when $E > \Lambda$ so that the density of states is positive; in the gap the plus sign must be chosen, while in the two regions outside the energy bands the minus sign is the correct one.

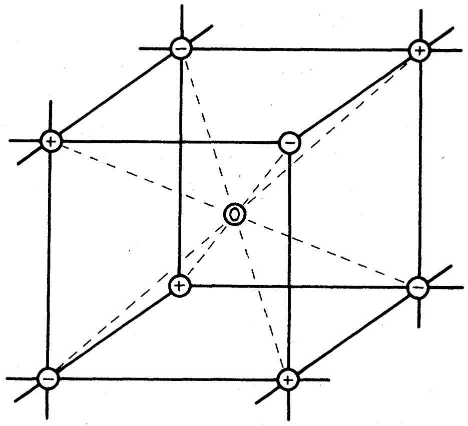

FIG. 1. Cluster of atoms in the rocksalt structure, with an interstitial hydrogen impurity, labeled 0. A Bethe lattice is connected to the three dangling bonds of each atom.

III. RESULTS

The LDOS at the impurity obtained from (5), (6), and (8) consists essentially of two bands with a gap between $E = \pm\Lambda$ and outer edges at $E = \pm(\Lambda^2 + 20V^2)^{1/2}$, as given by the Bethe lattice, and one localized state in the gap. The position as well as the weight of this state are determined by the parameters V^+ and V^-. Equations (3) and (8) clearly show that in the no-coupling limit, i.e., $V^+ = V^- = 0$, the LDOS at the defect consists only of a δ function of weight 1 at Λ_0 and no bands. The coupling via V^+ and V^- causes a change in the energy and the weight of the localized state: this state appears also at the ionic sites, decaying rapidly into the bulk. The relevant parameters for the defect model calculation are obviously V^+ and V^-, therefore the value of Λ must be specified. Since Λ is the diagonal matrix element of H_0, its value must be larger (but of the same order of magnitude) than the value of the nearest neighbors hopping integral V. We choose $\Lambda = 2V$ and for the model we are proposing, small changes in Λ are not relevant.

Calculations have been done for several values of the parameters involved in the problem.

A typical energy dependence of the LDOS at the impurity is shown in Fig. 2, which corresponds to $V^+ = 0.2$, $V^- = 0.4$, and $\Lambda = 2$, in units of V. Note that states in the continuum present sharp peaks at the four band edges. The peaks at $\pm\Lambda$ correspond to pure anion and cation states,[2] and since the perturbation term H' does not introduce any change to the diagonal terms of $H_0(\Lambda_0 = 0)$, they are present for all values of V^+ and V^-: these peaks decrease in intensity as V^+ and V^- increase, and they do not split off the continuum as in the case of the vacancy,[3] so that only one pole exists in the gap. The peaks at the outer edges increase in intensity as V^+ and V^- increase, up to some critical sets of values (for each V^+ there is a critical V^- and vice versa), for which δ-function states split off the outer band edges. A small increase in the value of V^+ or V^- from the set chosen in Fig. 3 causes a state to split from the upper band edge $[E = (24)^{1/2}]$, and this is the reason why an extremely sharp peak appears at this position. For example, for $V^+ = 0.2$ and $V^- = 0.6$, a pole of weight 7.2×10^{-3} appears just above the upper band, and another one of weight 1.1×10^{-3} just below the lower band. For other sets of values, only one of these states may be present. Of course for $|V^+|$ and $|V^-| \gg 1$, these states are quite far from the band edges, and their weights are not so small.

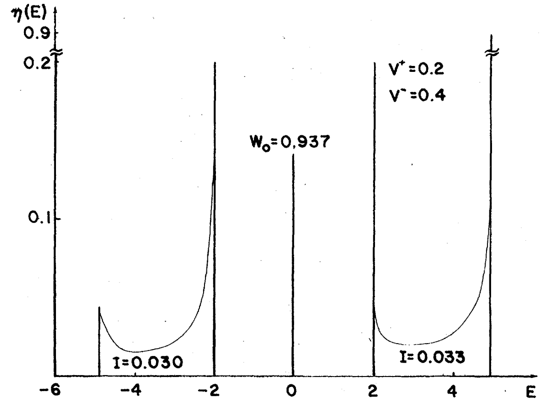

FIG. 2. Local density of states at the hydrogen site for the cluster–Bethe-lattice system in Fig. 1, for $\Lambda = 2$, $V^+ = 0.2$, and $V^- = 0.4$, in units of V. The vertical line represents a δ-function state of weight $W_0 = 0.937$, and the areas under the curves are indicated. A small increase in the value of V^+ or V^- from the chosen set causes a state to split from the upper band edge $[E = (24)^{1/2}]$ and that is why an extremely sharp peak appears there.

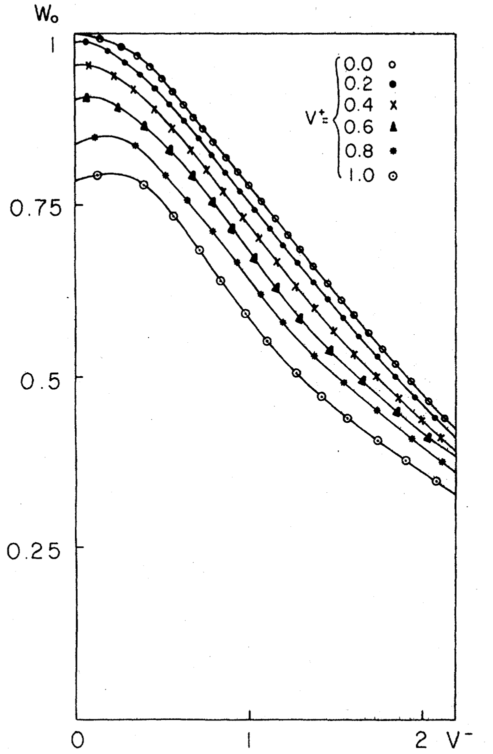

FIG. 3. Dependence of the weight of the pole at the hydrogen site on the parameters V^+ and V^-, given in units of V.

In Fig. 2, we also give the numerically integrated density of states for each band, and the weight of the pole at energy $P = -0.029$. The sum of these three values equals 1, which is the normalization condition. The position and weight of the pole in the gap depend not only on the absolute values of V^+ and V^-, but also on their relative sign. From (8), (9), and (10), we notice the following symmetry property of the poles P and residues W_0 of $\langle 0|G|0\rangle$ for $\Lambda_0 = 0$:

$$\begin{aligned} W_0(V^+, V^-, P) &= W_0(-V^+, -V^-, P) \\ &= W_0(-V^-, V^+, -P) \\ &= W_0(V^-, -V^+, -P) . \end{aligned} \tag{11}$$

Therefore, we just calculate the poles and residues of $\langle 0|G|0\rangle$ for positive values of the parameters, the other possibilities are easily obtained from this one. The position of the pole in the gap is near $\Lambda_0 = 0$ for small values of V^+ and V^-; it approaches the upper band edge for $V^+ \gg V^-$ in agree-

TABLE I. Theoretical and experimental (Ref. 17) values of $\eta = (a_H^0 - a)/a_H^0 = W_0 - 1$ [Eq. (13)]. The weight W_0 is calculated for values of the parameters V^+ and V^- estimated from qualitative arguments.

	NaCl			KCl			RbCl			NaBr			KBr			RbBr		
V^-		0.3			0.275			0.25			0.350			0.325			0.3	
V^+	0.15	0.2	0.25	0.125	0.175	0.225	0.1	0.15	0.2	0.15	0.2	0.25	0.125	0.175	0.225	0.1	0.15	0.2
W_0	0.964	0.959	0.952	0.970	0.966	0.960	0.976	0.972	0.967	0.953	0.948	0.942	0.961	0.956	0.951	0.968	0.964	0.959
$W_0 - 1$		−4.1%			−3.4%			−2.8%			−5.2%			−4.4%			−3.6%	
$(a_H^0 - a)/a_H^0$ [a]		−4.77%			−3.01%			−2.58%			−8.29%			−5.88%			−5.03%	

[a] See Ref. 17.

ment with simple perturbation-theory arguments. The behavior of its weight (W_0) at the impurity as a function of the parameters is plotted in Fig. 3. For a fixed V^+, W_0 increases slightly with V^-, up to a value for which W_0 is maximum, thereafter W_0 decreases monotonically, tending to zero as its position approaches the band. The value of V^- for which W_0 is maximum increases with V^+.

The physical nature of the three possible poles that appear in the LDOS at the impurity can be understood in a very simple qualitative way. The pole in the gap is due to the pure hydrogen state $|0\rangle$, whose position Λ_0 and weight 1 are modified by the interaction with the crystal via V^+ and V^-. As $|V^+|$ and $|V^-|$ get bigger, this localized state penetrates more into the crystal, consequently W_0 decreases, and bulk states penetrate more into the impurity site, increasing the integrated density of states in the continuum. The poles outside the bands appear when $|V^+|$ and $|V^-|$ are large enough to perturb a bulk state as to cause its eigenenergy to be outside of the continuum. The nature of the state depends on the values of V^+ and V^-; it is more extended when its energy is near the edge of the band, and for big $|V^+|$ or $|V^-|$, its energy is far from the bands region, and it is essentially localized at the impurity and a few layers of neighbors around it.

IV. PROTON CONTACT TERM IN ALKALI HALIDES

In order to propose a physical model for the U_2 center in alkali halides, we must establish a criterion to choose the parameters appearing in the Hamiltonian.[2] For this kind of defect, H' in Eq. (3) can be regarded as a small perturbation with respect to H_0; i.e., $|V^+|$ and $|V^-|$ are expected to be of the order of $\frac{1}{10}\Lambda$. Once the criterion is established, it is possible to use the results for the electronic LDOS at the impurity site and to relate it to the proton isotropic hyperfine parameter in a spin-restricted scheme

$$a_H = \tfrac{8}{3}\pi g \mu_B g_p \mu_n |\Psi(\vec{r}_p)|^2 , \tag{12}$$

where g is the free-electron g factor, g_p is the proton g factor, μ_B is the Bohr magneton, μ_n is the nuclear magneton, and $\vec{r}_p$ is the proton position. Since the method used here does not yield $\psi(\vec{r})$ directly, we are only able to obtain relative values of a; the results are given relative to the free hydrogen isotropic parameter: $a_H^0 = 1420$ MHz.

For the present one-orbital-per-site model, in these crystals the lower band is doubly occupied, the upper band is empty, and the localized state is singly occupied. Since spin polarization is not taken into account here the whole contribution to Eq. (12) comes from the unpaired electron wave function, so that

$$a_H/a_H^0 = W_0 . \qquad (13)$$

Our choice of normalization relative to the free hydrogen atom implies necessarily $a_H/a_H^0 < 1$. This is the case for the compounds we are interested in therefore the choice is adequate.

We now present very simple arguments based on lattice parameters and ionic radii[17,18] leading to the trend of V^+ and V^- for two families of alkali halides: (i) NaCl, KCl, RbCl; and (ii) NaBr, KBr, RbBr. Within each family, the lattice parameter increases with the alkali atomic number, being smaller for the Na halide. The absolute value of the hydrogen-halogen hopping integral (V^-) is expected to decrease with the distance between them, since their radii remain essentially constant, so that in each family $|V^-|$ should decrease from the Na to the Rb halides. This qualitatively accounts for the trend of V^- in each family. Two different contributions must be considered for the behavior of $|V^-|$ as we change families: the increase in the ionic radius, which increases $|V^-|$, and the increase in the lattice parameter, which decreases it from each cloride to the corresponding bromide. From the values presented in the literature,[17,18] we notice that the increase of the ionic radius is roughly twice the increase in the lattice parameter for each of the three members of the families, therefore the former effect must dominate: $|V^-|$ increases from the chlorides to the bromides. Since the cation radius is always smaller than the anion radius, $|V^+| < |V^-|$ in all cases: we make no other assumptions about the trend of V^+. Finally, we keep $\Lambda = 2V$ unchanged for all the crystals, and express all energies in units of V.

We use the value of the proton contact term in NaCl to guess reasonable values for V^+ and V^- for this crystal, assuming they have the same sign. Based on the above arguments we obtain values for the parameters in the other compounds and calculate W_0 for all of them. Results are shown in Table I, together with the experimental value[17] for $(a_H^0 - a_H)/a_H^0$. The experimentally observed trend can be understood completely by the behavior of V^-: for each compound we vary V^+ over a relatively wide range of values, just keeping it smaller than V^-, and the results are not as sensitive to this change in V^+ as to much smaller changes in V^-. Within each family, V^- is decreased from the Na to the Rb halides so that V^- is roughly proportional to the inverse of the lattice parameter: the product of the lattice parameter by V^- is ~0.8 Å for the chlorides and ~1 Å for the bromides. The increase in V^- from NaCl to NaBr is taken arbitrarily.

There is no *a priori* reason to choose V^+ and V^- to have the same sign (results in Table I do not change if they are both taken negative). From (11), we see that W_0 depends not only on the absolute values but also on the relative signs of V^+ and V^-. We calculated W_0 for V^+ and V^- with opposite signs, keeping the same absolute values as in Table I: all the results change by less than 0.3% therefore for this range of values, the relative sign of the parameters does not affect our conclusions.

V. CONCLUSIONS

Using a very simple theoretical method, and a model Hamiltonian involving parameters which are estimated by purely qualitative arguments, we are able to obtain a fairly good quantitative description for the proton contact interaction in several alkali halides.

The limitations of the present approximations become apparent when we try to apply the same scheme to calculate the Fermi contact term for the other nuclei.

The whole contribution for this term still comes from the unpaired electron, because we do not include in the Hamiltonian parameters to simulate spin polarization, which could differentiate spin-up and spin-down bands. Thus, as the lower band is fully occupied, there is no contribution for the contact term from the extended states. We have calculated the weight of the pole at the first shell of hydrogen neighbors, and thus the contribution for the contact term arising from the impurity state. We have obtained the correct order of magnitude for the contact term in the cation nuclei, but in the case of the anion, our results are orders of magnitude smaller than the experimental ones, showing that the former agreement must be regarded as purely accidental. To neglect the contribution for the contact interaction due to spin polarization is a reasonable approximation for the proton, but not for the other nuclei.

The present results regarding the energy position of the localized level site with respect to the s bands in the crystal (see Fig. 2) are in good agreement with calculations for the electronic structure of this defect using different schemes[10,19]; this supports our choice for the parameter Λ_0. Since our basis is restricted to s-like orbitals, we cannot expect to reproduce the experimentally observed optical transitions: any realistic treatment of such properties should include the p states. Improvements on the present model can be obtained by the inclusion of p states to our basis, as well as the consideration of spin-polarization effects. Such improvements would considerably increase the number of parameters involved in the calculation, without modifying significantly the results reported in this work.

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