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FOR THE F-CENTER IN ALKALI-HALIDES

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ABSTRACT. The electronic structure of the F-center in alkali-halides with the NaCl structure has been studied using the Cluster-Bethe Lattice method. The central cluster has been taken as constituted by the vacancy and the nearest- and second-neighbors to it, respectively cations and anions. The optical transitions have been calculated and compared to experimental data on the location of the peak of the F-absorption band. The agreement obtained indicates that this method may be used to study properties of this defect in alkali halides.

RESUMO. A estrutura eletrônica do centro F em halogenetos alcalinos com a estrutura do NaCl foi estudada utilizando-se o método Cluster-Rede de Bethe. O cluster central foi tomado como sendo constituído pela vacância, pelos cátions primeiros vizinhos e pelos ânions segundos vizinhos à mesma. As transições óticas foram calculadas e comparadas com os dados experimentais sobre o pico da banda F de absorção. A concordância obtida indica que este método pode ser usado para o estudo de propriedades deste defeito em halogenetos alcalinos.

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I. INTRODUCTION

The Cluster-Bethe Lattice (CBL) method, in a one-particle Green's function formalism, has been used in the study of several properties of solids, such as electronic density of states in crystalline and amorphous solids [1,2] and in alloys [3,4], spin wave spectra in dilute ferromagnets [5] and point defects in crystalline solids [6,7]. It consists in dividing the system under consideration in two parts: a cluster, where one tries to represent the relevant features as realistically as possible, and the rest of the solid, which is simulated by the topological structure called "Bethe lattice" (BL). The BL keeps the connectivity and coordination number of the original system, but has no rings of bonds; the visualization of such arrangement explains its alternative name of "Cayley tree". The characteristics of the BL allow one to solve exactly the infinite system of coupled linear equations connecting the matrix elements of the Green's function and to obtain, for instance, the electronic density of states (DOS). In this case, the fact that the BL preserves the infinite connectivity of the system is responsible for the appearance of bulk states in the DOS.

The purpose of this work is to present a theoretical study of the electronic structure of the F-center (anion vacancy with a trapped electron) in alkali-halides with the NaCl structure by the CBL method. The F center is probably the most studied point defect, a large amount of experimental and theoretical work being available [8,9,10]; here we shall be particularly interested in studying the position of the

peak of the F-absorption band. A simple model for the F-center describes the trapped electron in a spherically symmetric potential due to the absence of the anion at the origin, simulating the effect of the crystal by a dielectric constant and by an electronic effective mass [8]; the F-absorption band is then associated to the $1s-2p$ transition. More refined models consider the influence of the crystal on the F-electron in a more realistic way, including ion-size corrections, based on the theory developed by Bartram, Stoneham and Gash [11], and using flexible trial variational pseudo-wavefunctions as done by Harker [12]; recently, within the same approach, Ong and Vail [13] have incorporated possible lattice distortion effects in a self-consistent manner. These models provide reasonably good agreement with the experimental data concerning the position of the peak of the F-band [8]. One of the advantages of the MFP method over the previously mentioned approaches is that, besides incorporating in a simple way the correct local symmetry of the defect, it also provides information concerning the bulk properties as well as the localized electronic states associated to the defect. Also, its characteristic of describing in greater detail one region of the crystal, makes this method specially suitable for the study of point defects, allowing the region near the center of the defect to be treated in a more rigorous way.

The application of this method to the U-center in alkali-halides [7] yields reasonable results for the proton contact interaction, by means of a Hamiltonian whose

parameters are estimated on the grounds of qualitative arguments. In the present work simple qualitative assumptions are used to evaluate the parameters appearing in the Hamiltonian based on previous band structure calculations relative to the perfect crystals and on atomic data.

In section II, we present the model Hamiltonian for the F-center in alkali-halides, discussing the choice of the basis functions and the symmetry of the defect states. In section III, the electronic structure of the F-center is obtained and the optical transitions are compared with experiment. Finally, in section IV we present our conclusions.

II. MODEL HAMILTONIAN AND CBL CALCULATIONS FOR THE F-CENTER IN ALKALI-HALIDES

Taking Dyson's equation for the one-electron Green's function $G(E)$ [14]

$$(E - H)G(E) = I, \quad (1)$$

which can be written in matrix form relatively to a complete orthonormal basis $\{|b\rangle\}$ as

$$E\langle b|G|b'\rangle = \delta_{bb'} + \sum_{b''} \langle b|H|b''\rangle \langle b''|G|b'\rangle; \quad (2)$$

the electronic density of states (DOS) for the system is given by [14]

$$N(E) = -\frac{1}{\pi} \text{Im tr } G(E) \quad (3)$$

Considering specifically the study of point defects in ionic crystals, an adequate approximation for the basis $\{|b\rangle\}$ is the set of atomic orbitals centered on each crystalline site. Representing by $|ij\rangle$ the j -th orbital relative to the ion localized on site i , the orthonormality condition $\langle ij|i'j'\rangle = \delta_{ii'}\delta_{jj'}$, means that on each site different atomic orbitals are orthogonal (which is an exact statement), and that the overlap between orbitals centered on different sites is zero (which is a good approximation for the valence orbitals of the elements in ionic crystals).

With this choice of basis, the local density of states (LDOS) on site i , $N_i(E)$, is given by:

$$N_i(E) = -\frac{1}{\pi} \text{Im} \int \langle ij|G|ij\rangle$$

We write the orbital representation of the Hamiltonian as

$$H = \sum_{ij} U_{ij} |ij\rangle\langle ij| + \sum_{i,i',j,j'} V_{ij i'j'} |ij\rangle\langle i'j'|$$

where the U_{ij} 's are associated to the "eigenenergies" of the orbitals $|ij\rangle$ (i.e., neglecting interactions between orbitals, each orbital $|ij\rangle$ would be an eigenstate of H , associated to the eigenvalue U_{ij}); and the terms $V_{ij i'j'}$ represent the interaction between orbitals $|ij\rangle$ and $|i'j'\rangle$. We shall take only nearest-neighbour interactions into account. Also, we shall restrict the basis, for each site, to atomic orbitals which may be relevant for the optical transitions of the system; these only involve electronic

states near the Fermi level. Such crystalline states come mainly from the atomic valence orbitals, the inner orbitals giving no relevant contribution. For simplicity, our basis is constituted by one s orbital per ionic (cation or anion) site; for the cations this is a good assumption, since the alkali valence electron occupies an s orbital. Although the halogen valence electron has p symmetry, giving rise to a completely filled p-like band in alkali-halides, we describe it as s-like, and, as commented below in this section, the exclusive use of s-orbitals is a good approximation; the inclusion of p-orbitals in the basis brings no relevant new information.

Since the orbitals are spherically symmetric, the nearest-neighbour interaction is isotropic and is denoted here by V ; the origin of the energies for the perfect crystal can be chosen in such a way that $U_i = +U$ if $|i\rangle$ is a cationic orbital, and $U_i = -U$ if $|i\rangle$ is an anionic one. Hence, the Hamiltonian for the perfect crystal is written

$$H = \sum_i \pm U |i\rangle\langle i| + V \sum_{i,i'} |i\rangle\langle i'|, \quad (6)$$

nearest neighbours

the + or - sign chosen in accordance with the above considerations.

With the crystalline structure simulated by the Cluster-Bethe Lattice approximation, this Hamiltonian yields a DOS consisting of two bands of equal width, located in the energy intervals $(-[U^2 + 20V^2]^{1/2}, -U)$ and $(U, [U^2 + 20V^2]^{1/2})$, and no localized states, as reported by Yndurain and Joannopoulos [2].

For the crystal containing the F-center, we still

keep the single s-orbital per site basis, including the site of the vacancy; if this is denoted by 0, the six cationic first-neighbour sites by 1 and so on, according to Fig. 1, the Hamiltonian we use is written as

$$H = \sum_i U_i |i\rangle\langle i| + \sum_{ii', \text{ nearest neighbours}} V_{ii'} |i\rangle\langle i'| \quad (7)$$

where

$$U_i = \begin{cases} \delta & \text{if } i = 0 \\ U - U_F & \text{if } i = 1 \\ \pm U & \text{if } i \text{ is respectively a cationic or anionic} \\ & \text{site, and } i \neq 0, 1. \end{cases}$$

$$V_{ii'} = \begin{cases} V_F & \text{if } i = 0 \text{ or } i' = 0 \\ V & \text{otherwise} \end{cases}$$

In this way, we keep the same origin for the energies as in the perfect crystal, and introduce corrections only to nearest-neighbours, which is reasonable due to the fact that the F-center is neutral relative to the crystal. The discussion of the values of all parameters is presented in sec. III.

For the present calculations, we use the 18-atom plus vacancy cluster shown in Fig. 1, with a Bethe lattice attached to each dangling bond (one in ions labelled 1 and four in ions labelled 2). The electronic structure of the defect is obtained from the diagonal matrix elements of the Green's functions; for the cluster in Fig. 1, the equations relative to orbital $|0\rangle$ are:

$$\begin{aligned}
(E - \delta) \langle 0|G|0 \rangle &= 1 + 6V_F \langle 0|G|0 \rangle \\
(E - U + U_F - VT^+) \langle 1|G|0 \rangle &= V_F \langle 0|G|0 \rangle + 4V \langle 2|G|0 \rangle \quad (8) \\
(E + U - 4VT^-) \langle 2|G|0 \rangle &= 2V \langle 1|G|0 \rangle
\end{aligned}$$

in which T^\pm are the transfer functions [2] which represent the effective interaction with a heteropolar Bethe lattice along one bond on a positive or negative ion, respectively. For the NaCl structure, they are given by [2]

$$T^+ = \frac{E''}{10V} + \frac{[E'E''(E'E'' - 20V^2)]^{1/2}}{10VE'}; \quad T^- = \frac{E'}{E''} T^+ \quad (9)$$

where $E' = E + U$ and $E'' = E - U$; the sign of the square root is chosen to be the plus sign in the lower band and in the gap, and the minus sign elsewhere, according to ref. [6]. With

$$\begin{aligned}
E_1 &\equiv E + U - 4VT^- \\
E_2 &\equiv E - U + U_F - VT^+ \\
E_3 &\equiv E - \delta
\end{aligned} \quad (10)$$

The solution for eqs. (8) is

$$\langle 0|G|0 \rangle = \frac{E_1 E_2 - 8V^2}{E_3 (E_1 E_2 - 8V^2) - 6E_1 V_F^2} \quad (11)$$

Analogously, from the equations relative to orbitals $|1\rangle$ and $|2\rangle$, we get:

$$\langle 1|G|1 \rangle = E_1 \frac{E_3 [(E_1 E_2 - 5V^2)^2 - 5V^4] - E_1 V_F^2 (5E_1 E_2 - 14V^2)}{(E_1 E_2 - 2V^2) (E_1 E_2 - 4V^2) [E_3 (E_1 E_2 - 8V^2) - 6E_1 V_F^2]} \quad (12)$$

$$\langle 2|G|2 \rangle =$$

$$= \frac{E_3 \{ (E_1 E_2 - 4V^2)^2 (E_1 E_2 - 2V^2) - 2E_1 E_2 V^2 (E_1 E_2 - 3V^2) \} - E_1 V_F^2 \{ 6(E_1 E_2)^2 - 28V^2 E_1 E_2 + 28V^4 \}}{E_1 (E_1 E_2 - 2V^2) (E_1 E_2 - 4V^2) [E_3 (E_1 E_2 - 8V^2) - 6E_1 V_F^2]}$$

(13)

Expressions (11), (12) and (13) yield an energy spectrum which consists of two bands of same width and gap as the perfect crystal ones, and a set of δ -function or F-center states.

Since the model hamiltonian has cubic symmetry with respect to the center of the vacancy, the solutions for the F-center states must be classified according to the irreducible representations of the group O_h . Theories which describe the vacancy by a spherically symmetric potential associate the F-band to the optical transition from the fundamental 1s to the excited 2p state; here we expect to get in the gap region, the ground state with Γ_{1g} symmetry and an excited state with Γ_{4u} symmetry, the optical transition occurring between them. Excited states of different symmetry take no part in the F-absorption, although they might play an important role in the F-center relaxed excited state, and in the emission band.

The F-center states correspond to the poles of $\langle 1|G|1 \rangle$ or $\langle 2|G|2 \rangle$ which appear in the gap region; of course, states of symmetry other than Γ_{1g} can not be obtained from $\langle 0|G|0 \rangle$. The symmetry of each state can be determined through the analysis of the non-diagonal matrix elements of the Green's function, which give the wave function amplitude

ratios at different sites [15]. The roots of the denominator of (12) which appear in the gap region are associated with states of the following symmetry:

$$\begin{aligned}
 E_3(E_1E_2 - 8V^2) - 6E_1V_F^2 &= 0 & \rightarrow \Gamma_{1g} \\
 E_1E_2 - 2V^2 &= 0 & \rightarrow \Gamma_{3g} \\
 E_1E_2 - 4V^2 &= 0 & \rightarrow \Gamma_{4u}
 \end{aligned}
 \tag{14}$$

Therefore, besides the two energy bands in the DOS, there are three localized states in the gap, of symmetry Γ_{1g} , Γ_{3g} and Γ_{4u} in order of increasing energy. There is still another Γ_{1g} state above the conduction band, which comes mainly from an antibonding combination of the vacancy orbital and its nearest neighbors, and plays no role in the absorption process we are interested in.

Other models for the F-center yield an excited Γ_{1g} state whose energy is close to the Γ_{4u} state; the inclusion, in our model, of p-like orbitals in the nearest neighbors of the vacancy, directed along the [100] direction, would result in such a state, but we do not attempt that here.

It is to be noticed that, in a calculation with a 6-atom plus vacancy cluster, the states Γ_{3g} and Γ_{4u} are degenerate, the degeneracy being lifted only with the inclusion of more atoms in the central cluster. The inclusion of three p-like orbitals, instead of the s-like ones, in the anionic sites, does not lift the Γ_{3g} - Γ_{4u} degeneracy even with a 18-atom cluster; this comes from the fact that the symmetry of the crystal imposes some selection rules for the matrix elements of the hamiltonian, making the interaction between

such orbitals too much directioned, and this implies in a loss of information about the local symmetry.

Such selection rules are also responsible for the fact that the model with p-orbitals in anionic sites yields two bands with the same width, contrarily to what could be expected in analogy with other band calculations, in which the inclusion of p-orbitals in the basis gives rise to a p-band narrower than the s-band.

Also, the crystalline symmetry keeps the p_x , p_y and p_z bands completely degenerate, making it reasonable to describe their average as an s-band.

III. RESULTS AND DISCUSSIONS

In this section, we estimate the parameters introduced in the model Hamiltonian (7) based on simple qualitative arguments, and from these estimated values we determine the electronic structure of the alkali-halides and the F-center transition energy.

The "perfect crystal" parameters - U and V - can be determined from the width $(\sqrt{U^2 + 20V^2} - U)$ and the gap between the bands $(2U)$ in the perfect crystal. We have taken the values of the gap and the width of the lowest s-like conduction band from band structure calculations for the alkali-halides [16,17,18,19,20]; typical values for the gap are between 6 eV and 10 eV, and for the band widths between 2 eV and 4 eV. The conduction band is chosen because it is consistent with the kind of orbitals used

in our basis (s-type). For all crystals studied the values obtained for U are between 3 eV and 5 eV, and for V between 1 eV and 1.5 eV, as shown in Table I.

For the evaluation of the parameter δ , it is convenient to choose as reference energy the lower continuum limit. We can locate the origin used in our calculations in the following manner: with respect to this new reference, the energies of the atomic orbitals are just the negative of the ionization energies, and can be obtained from atomic data tables (21). Assuming the corrections in the self-energies of the atomic orbitals due to crystalline effects to be Madelung-type, with the polarizability of the medium taken into account through a dielectric constant, it is expected that such corrections shift symmetrically the energies of the cationic and anionic orbitals. Then, the position of the previously chosen origin is obtained by the arithmetic average between the ionization energies of the (ns) alkaline and (mp) halogen orbitals (see Fig. 2). Of course, the bound character of the vacancy orbital is exclusively due to the presence of the crystal, which lowers its energy from the continuum by a correction which we also suppose to be Madelung-like, allowing δ to be determined, as shown in Fig. 2. We write this correction as $\Delta E^V = -\alpha_M \frac{e^2}{\epsilon a}$, where $\alpha_M = 1.75$ is the Madelung constant of the NaCl structure, a is the nearest-neighbour distance and ϵ is the static dielectric constant of the substance. The choice of the static dielectric constant in the evaluation of δ is discussed below.

The parameter V_F is estimated considering the fact that the F-electron is less localized than an anionic one, therefore we choose arbitrarily V_F equal 1.5 V, for all the chlorides we study.

For the other halides, V_F is assumed to vary inversely with the lattice parameter, and is obtained from the values of V_F for the chlorides.

Finally, the neutrality of the F-center relative to the lattice and the fact that the defect electron is not entirely confined inside the vacancy 1st neighbors shell ensure that the value of U_F must be small compared to U and positive. We take $U_F = 0.10$ eV in all cases.

The values obtained for the parameters used in our calculation are listed in Table I. The result for the L.D.O.S. at a cation site nearest to the vacancy in KCl is given in Fig. 3, and this is a typical result for all compounds we studied. The energies of the poles given by Eqs. (14) are presented in Table II.

As discussed in Sec. II, we associate the optical transition of the F-center with the one between the states of symmetry Γ_{1g} and Γ_{4u} found in the gap region. We call $\Delta E = E_{\Gamma_{4u}} - E_{\Gamma_{1g}}$ the energy of the F-center optical absorption, and in Table III we compare these values with the experimental values obtained from the position of the peak of the F-absorption band.

It is interesting to notice that, although there exists some arbitrariness in the evaluation of the parameters, the results presented in Table III are quite stable relative

to their variations: modifications of $\pm 50\%$ in the values of U , V and V_F yield maximum variations of about 15% in the values obtained for the optical transitions. The small value of U_F is responsible for the fact that the excited states E_{3g} and E_{4u} lie very near the bottom of the conduction band, which is in agreement with experiment [9]. In the limit $U_F \rightarrow 0$, both E_{3g} and E_{4u} merge into the conduction band, becoming a square root singularity at $E = U$ [2].

The evaluation of the parameter ϵ is more significant in the results, and it is estimated using the static dielectric constant value in the calculation of the Madelung energy. The static dielectric constant overestimates the polarization of the medium; the use, for example, of the high frequency dielectric constants yields smaller values of ϵ , which lowers the ground state energy. It is interesting to notice that the transition energies given in Table III are typically smaller than the experimental values, while the values obtained from calculations using the high frequency constants yield results typically above the experimental ones by errors of the same order. It is also verified that, in each family of halides, the deviation from the experimental value increases with the atomic number of the halide, which is probably due to the fact that for heavier nuclei the use of static dielectric constants is less justified.

Another possible test for our model consists in obtaining informations about the wave functions of the discrete states, comparing our results to experimental data

of hyperfine contact parameters. It is important to note that the CBL method is not suited to describe wave functions in detail; we obtain the weight of the states associated to the discrete levels in the L.D.O.S. of a given site by calculating the residues of the poles of the diagonal matrix element of the Green's function relative to that site:

$$W_i(E_0) = \text{res}_{E=E_0} \langle i | G | i \rangle \quad (15)$$

The weights of the localized states on sites labelled 0, 1 and 2 in Fig. 1 are given in Table IV. From eq. (11), $W_0(E_{3g}) = W_0(E_{4u}) = 0$. If we call R_i the relation between the square of the F-electron wave function respectively on sites 1 and 2, obtained experimentally from the hyperfine contact parameters [22], we can compare it to $R_2 = W_1(E_{1g})/W_2(E_{1g})$ obtained from our calculations. For the compounds we studied, R_2/R_1 varies between 2 and 6, indicating no order of magnitude contradiction between our results and experiment. Other contributions to the contact interaction, such as spin polarization and direct overlap among neighbour wave functions, which are not included here, must be taken into account in a more realistic model for the contact parameter.

IV. CONCLUSIONS

The results obtained in this work indicate that the CBL method is able to describe in a reasonable manner the electronic structure and the optical transitions of the F-center. Although there is a considerable number of parameters in the model, all of them can be estimated based

on simple arguments. The stability of the results relative to variations in the values of the parameters is a point favorable to the consistency of the model. Besides that it is to be noticed that some features, as the fact that the excited states lie very near the conduction band, and the symmetries of discrete states, are properly incorporated by the characteristics of the model, with no need to be explicitly included.

Of course, the method cannot describe correctly properties like hyperfine interactions, which depend on details of the wave functions; even so, the results obtained in the treatment of such instructions indicate an order-of-magnitude agreement.

Relative to the specific problem of the F-center, some aspects might be improved such as a larger set of basis functions, as for instance one s- and three p-orbitals per anion.

As mentioned, the inclusion of p-orbitals in the nearest-neighbours to the vacancy, would give rise to a F_{2g} state with energy near to the F_{4d} state; the hybridization between these states, yielding a "relaxed excited state", would explain the relatively long half-life ($\sim 10^{-6}$ sec) of the F-center excited state. The study of the F-emission band might be started from the convenient "relaxation" of some parameters used here.

TABLE CAPTIONS

Table I - Nearest-neighbour distances (a), gap (g) and conduction band widths (c); other quantities are defined in the text. a in angstroms, all other quantities in eV.

Table II - Calculated energies of the δ -function states, relative to the origin defined in the text. Units are eV.

Table III - Calculated (ΔE) and experimental (ΔE_{exp}) values for the optical transition of the F-center. Units are eV.

$$\epsilon \equiv (\Delta E - \Delta E_{\text{exp}}) / \Delta E_{\text{exp}}$$

Table IV - Weights of the δ -function states respectively on sites 0 (W_0), 1 (W_1) and 2 (W_2) as defined in Fig. 1.

FIGURE CAPTIONS

Fig. 1 - 18-atom cluster with a central vacancy, used in the F-center calculations. A Bethe lattice is connected to each dangling bond.

Fig. 2 - Energy diagram for the calculation of the parameter δ .

Fig. 3 - LDOS at a cation nearest neighbour to the vacancy in KCl. The heights of the bars are proportional to the weights of the δ -function states.

TABLE I

	a	g	c	U	V	V_F	U_F	δ
KCl	3.14	8.70 ^[16]	2.3 ^[16]	4.35	1.12	1.68	0.10	7.18
KBr	3.29	7.30 ^[16]	2.6 ^[16]	3.65	1.13	1.62	0.10	6.62
KI	3.53	6.30 ^[16]	2.3 ^[16]	3.15	0.97	1.29	0.10	6.06
NaCl	2.81	8.75 ^[17]	3.9 ^[17]	4.38	1.57	2.36	0.10	7.78
NaBr	2.98	7.10 ^[18]	2.5 ^[18]	3.55	1.10	1.56	0.10	7.28
NaI	3.23	5.98 ^[19]	3.4 ^[20]	2.99	1.26	1.64	0.10	6.78

TABLE II

	$E_{\Gamma_{1g}}$	$E_{\Gamma_{3g}}$	$E_{\Gamma_{4u}}$
KCl	2.201	4.328	4.341
KBr	1.815	3.631	3.642
KI	1.869	3.129	3.141
NaCl	1.563	4.367	4.375
NaBr	2.049	3.531	3.542
NaI	1.656	2.977	2.985

TABLE III

	ΔE	ΔE_{exp}	$\%$
KCl	2.14	2.18	- 1.8 %
KBr	1.83	1.97	- 7.1 %
KI	1.27	1.72	-26.2 %
NaCl	2.81	2.63	+ 6.8 %
NaBr	1.50	2.36	-36.4 %
NaI	1.32	2.04	-35.3 %

TABLE IV

	Γ_{1g}			Γ_{3g}		Γ_{4u}	
	W_0	W_1	W_2	W_1	W_2	W_1	W_2
KCl	0.348	0.085	0.006	0.125	8×10^{-5}	0.090	5×10^{-5}
KBr	0.328	0.080	0.007	0.110	7×10^{-5}	0.075	4×10^{-5}
KI	0.290	0.085	0.006	0.125	10×10^{-5}	0.087	7×10^{-5}
NaCl	0.357	0.069	0.010	0.078	3×10^{-5}	0.048	2×10^{-5}
NaBr	0.277	0.086	0.007	0.114	7×10^{-5}	0.077	5×10^{-5}
NaI	0.267	0.072	0.008	0.082	5×10^{-5}	0.050	2×10^{-5}

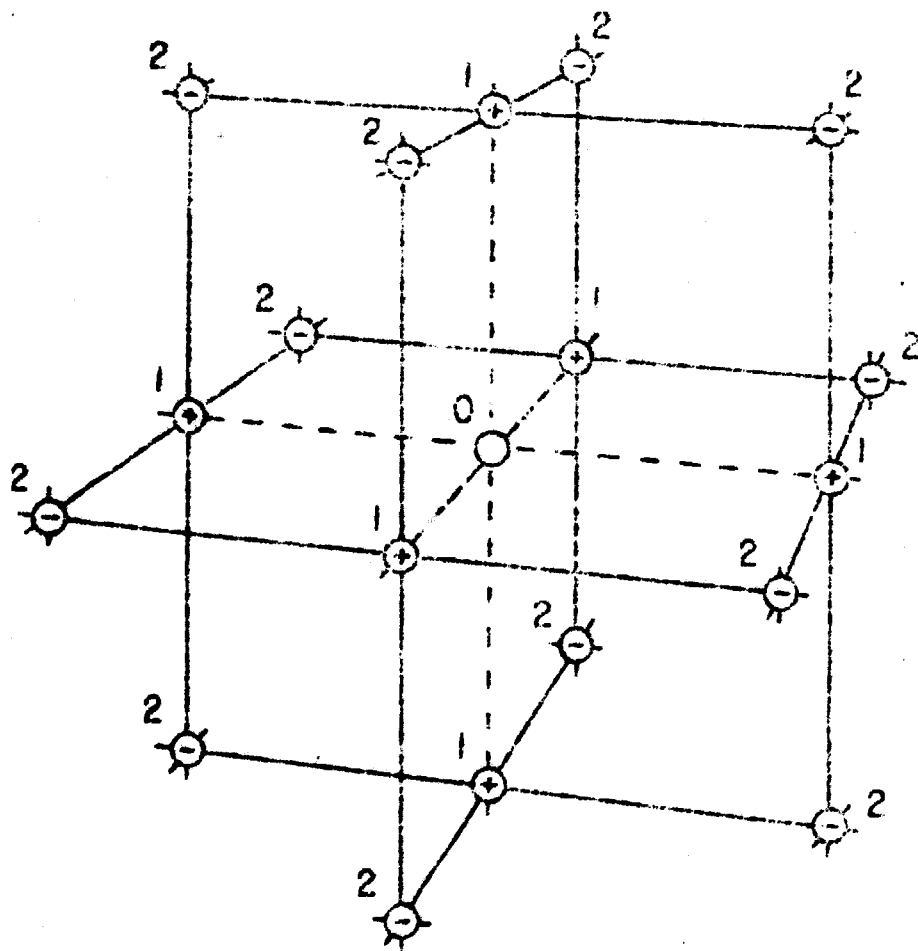


FIG. 1

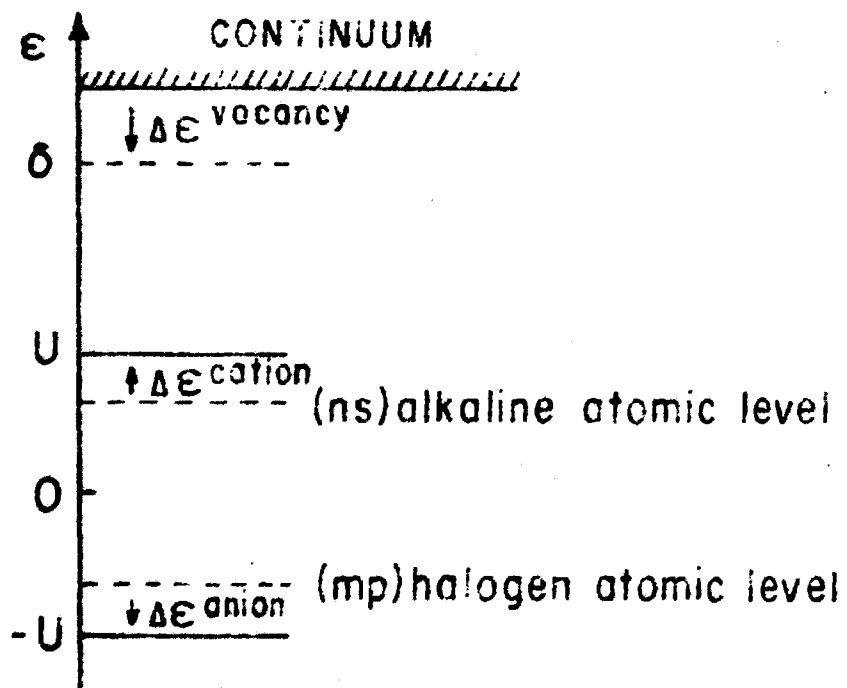
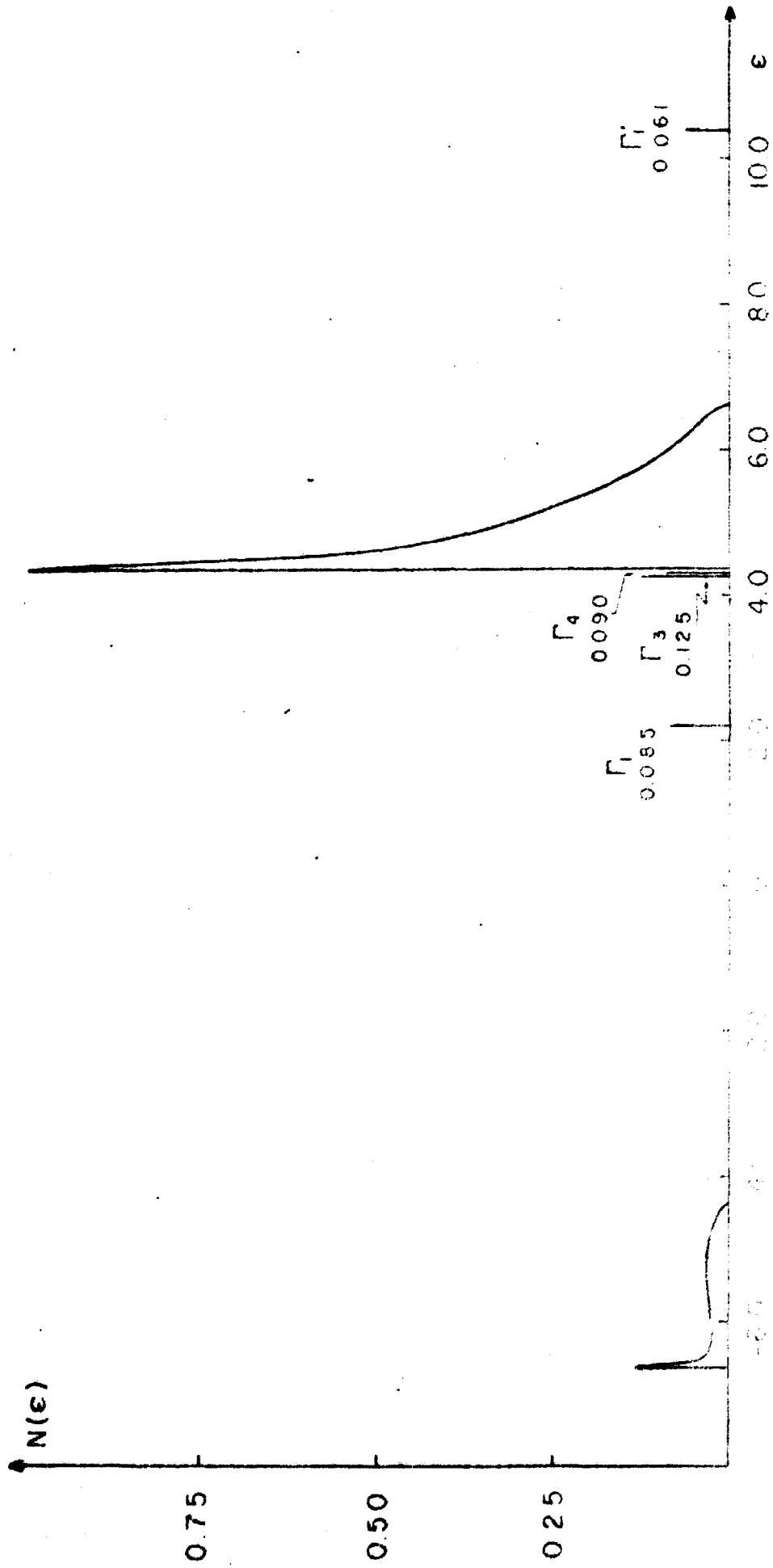


Fig. 1



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