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Giant binding of D^- centers in polar crystals

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It is shown that, due to the electron-LO phonon interaction, the ratio of the binding energy of D^- ions to that of donors (D^0) can be as much as an order of magnitude greater in strongly polar materials than in nonpolar crystals. A key role in the binding enhancement is played by the attraction between the electrons and the static polarization charge which they induce near the center of the ion. Estimates are given for D^- binding energies in AgBr and AgCl.

I. INTRODUCTION

It is well known that in a polar crystal characterized by an LO frequency ω, a slowly moving particle of band mass m induces around itself a ball of lattice polarization charge of radius $r_0=(\hbar/2m\omega)^{1/2}$, becoming a polaron. The interaction between two such particles with charge q_1 and q_2, which are separated by distances comparable to or smaller than r_0 is not given in general by a universal potential energy (for example, $q_1q_2/\epsilon_0 r_{12}$, which is valid for free particles at large separations r_{12}), but depends upon the quantum state of the interacting particles. This makes even the simplest interacting polaron systems hard to handle. As an example, the determination of the exciton ground-state energy in polar crystals in the simplest band model (parabolic conduction and valence bands) has attracted considerable theoretical interest for a number of years and is not yet a closed subject.[1,2]

Much less attention has been paid, however, to calculating the interactions between polarons of the same charge. That such interactions might be important experimentally was first suggested by Petelenz and Smith,[3] who noted that the two electrons bound in a D^- center in the polar semiconductor CdS are separated by distances typically of the order of r_0 so that, in analogy to the exciton case, the mutual repulsion between the electrons might not be well approximated by $e^2/\epsilon_0 r_{12}$.

In this paper the binding of D^- centers is calculated as a function of the two dimensionless parameters of the problem, the Fröhlich coupling constant α and R, the ratio of the hydrogenic rydberg to $\hbar\omega$. These quantities are defined by

$$\alpha=e^2/(2r_0\hbar\omega)(1/\epsilon_\infty-1/\epsilon_0) \ ,$$
$$R=me^4/(2\epsilon_0^2\hbar^3\omega)=[e^2/(2r_0\hbar\omega)(1/\epsilon_0)]^2 \ . \tag{1}$$

It is shown that in the D^-, unlike in the exciton, a central role in the binding at large α is played by the induced *static* lattice polarization charge.[4]

II. COMPUTATION OF D^- BINDING ENERGIES

In polaron units (lengths in units of r_0, energies in units of $\hbar\omega$) the Fröhlich Hamiltonian for a D^- center can be written

$$H=H_0+\frac{2\alpha}{r_{12}}+\sum b_k^\dagger b_k + \sum v_k\{[\exp(-i\vec{k}\cdot\vec{r}_1)+\exp(-i\vec{k}\cdot\vec{r}_2)]b_k^\dagger+\text{H.c.}\} \ ,$$
$$H_0=-\nabla_1^2-\nabla_2^2-\beta/r_1-\beta/r_2+\beta/r_{12} \ , \tag{2}$$

where $\beta=2R^{1/2}$,

$$v_k=(4\pi\alpha/\Omega)^{1/2}1/k \ ,$$

$b_k^\dagger$ is the creation operator for an LO phonon of wave vector $\vec{k}$, and Ω is the volume of the crystal in polaron units. In writing down H I have assumed that whereas the interaction of the electrons with the fixed central charge is proportional to $1/\epsilon_0$ (therefore to β), their mutual interaction is proportional to $1/\epsilon_\infty$ and therefore to $\beta+2\alpha$, since

$$1/\epsilon_\infty=1/\epsilon_0+(1/\epsilon_\infty-1/\epsilon_0) \ .$$

I attempt to estimate the ground-state energy of H by a variational method based on the ansatz of Buimistrov and Pekar (BP).[5] In this ansatz the lattice polarization consists of two parts, a part which depends upon the instantaneous positions of the electrons and a static part depending only upon the average electronic charge density. For both R and $\alpha \gtrsim 2$ the BP ansatz is known to be capable of giving energies close to the most accurate available when applied to the *donor* ground state.[6,7] The D^- trial function takes the form

$$\psi(r_1,r_2)\exp(-S_1)\exp(-S_2)|0\rangle \;,$$
$$S_1=\sum F_k(b_k^\dagger-b_k) \;, \tag{3}$$
$$S_2=\sum g_k\{[\exp(-i\vec{k}\cdot\vec{r}_1)+\exp(-i\vec{k}\cdot\vec{r}_2)]b_k^\dagger-\mathrm{H.c.}\} \;,$$

where F_k, which describes the static polarization charge, and g_k, which describes the polarization charge which follows the instantaneous position of the electron, are functions to be determined variationally. In Eq. (3) $|0\rangle$ is the phonon vacuum state.

For evaluating the expectation value of H in the wave function of Eq. (3) it is helpful to recognize

$$\begin{aligned}U^{-1}b_k^\dagger U&=b_k^\dagger-F_k\\&\quad-[\exp(i\vec{k}\cdot\vec{r}_1)+\exp(i\vec{k}\cdot\vec{r}_2)]g_k \;,\\U^{-1}\frac{1}{i}\nabla_{1,2}U&=\frac{1}{i}\vec{\nabla}_{1,2}+\sum\vec{k}g_k[\exp(-i\vec{k}\cdot\vec{r}_{1,2})b_k^\dagger\\&\quad+\exp(i\vec{k}\cdot\vec{r}_{1,2})b_k] \;,\end{aligned}\tag{4}$$

where $U=\exp(-S_1)\exp(-S_2)$ and use has been made of the assumption that g_k is a function only of $|\vec{k}|$. Applying the above formulas one obtains

$$\begin{aligned}\langle 0|U^{-1}HU|0\rangle=H_{\mathrm{eff}}=H_0+\frac{2\alpha}{r_{12}}+2\sum(g_k^2-2\nu_kg_k)\cos(\vec{k}\cdot\vec{r}_{12})+2\sum F_k(g_k-\nu_k)\,[\cos(\vec{k}\cdot\vec{r}_1)+\cos(\vec{k}\cdot\vec{r}_2)]\\+2\sum[(1+k^2)g_k^2-2\nu_kg_k+\tfrac{1}{2}F_k^2] \;.\end{aligned}\tag{5}$$

For each trial function $\psi(\vec{r}_1,\vec{r}_2)$ there is an optimal choice of g_k and F_k, found by minimizing the expectation value of H_{eff} in ψ with respect to these functions. Denoting the mean value of an arbitrary function f by

$$\langle f\rangle\equiv\int\psi^*f\psi\Big/\int\psi^*\psi$$

the optimum values of g_k and F_k are found to be

$$\begin{aligned}g_k&=\nu_k[1+\chi(k)]/[1+k^2+\chi(k)] \;,\\F_k&=-(g_k-\nu_k)U(k) \;,\\U(k)&=\langle\cos(\vec{k}\cdot\vec{r}_1)+\cos(\vec{k}\cdot\vec{r}_2)\rangle \;,\\\chi(k)&=\langle\cos(\vec{k}\cdot\vec{r}_{12})\rangle-\tfrac{1}{2}U(k)^2 \;.\end{aligned}\tag{6}$$

The variational estimate of the D^- ground-state energy obtained is

$$E_v^{(D^-)}=\langle H_0\rangle-2\alpha+\frac{4\alpha}{\pi}\int_0^\infty dk\frac{k^4\chi(k)}{[1+k^2+\chi(k)](1+k^2)} \;,\tag{7}$$

where use has been made of the relations

$$\sum\nu_k^2\rightarrow\frac{2\alpha}{\pi}\int_0^\infty dk \;,$$
$$\alpha=\sum\frac{\nu_k^2}{1+k^2} \;,$$
$$\frac{2\alpha}{r_{12}}=2\sum\nu_k^2\cos(\vec{k}\cdot\vec{r}_{12}) \;.$$

Before proceeding further, it is of interest to examine the weak binding-weak coupling limit of H_{eff}. In this limit one can neglect the static polarization charge introduced by the operator e^{-S_1} and set $F_k=0$ and $g_k=\nu_k/(1+k^2)$. The part of the trial function in Eq. (3) involving phonon operators then becomes very similar to the free-polaron ground-state trial function of Lee, Low, and Pines,[8] and H_{eff}, from Eq. (5), becomes

$$H_{\mathrm{eff}}\sim H_0+eV(r_{12}) \;,$$

where

$$V(r_{12})=\frac{e}{\epsilon_0r_{12}}+\frac{e}{r_{12}}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)(1-\tfrac{1}{2}r_{12})e^{-r_{12}} \;.$$

The potential $V(r_{12})$ is effectively weaker than the well-known Haken potential,[9] V_H, previously derived for the weak binding limit and given by

$$V_H=\frac{e}{\epsilon_0r_{12}}+\frac{e}{r_{12}}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)e^{-r_{12}} \;;$$

thus, H_{eff} gives stronger binding than does H_0+V_H.

In general, ground-state energies calculated from the Haken potential appear to be too deep for the exciton[10] and too shallow[3] for the D^- when compared to other, presumably more nearly exact, calculations. For the simple case of the polaron exciton composed of an electron and a hole of equal band mass, it is easy to show that the Haken potential leads to a correction in the unperturbed ground-state energy of order β^3 as $\beta\rightarrow0$ and $\alpha\rightarrow0$. This result is not consistent with Sak's finding[11] that there exists no correction to the exciton ground-state energy of order β^3 but only of order β^2 and β^4 in the weak-coupling, weak-binding limit. On the other hand, one can show that, consistent with Sak's result, $V(r_{12})$ gives a correction to the unperturbed ground-state energy of order β^4 in this limit. Thus there are good reasons to doubt that the Haken potential is correct for weak binding ($\beta << 1$) or quantitatively reliable for any binding strength.

Let us return now to the computation of the D^- binding energy for arbitrary β and note that Eq. (7) gives a rigorous upper bound to the ground-state energy of the D^- ion for each choice of ψ. In order to obtain an enhanced binding effect it appears essential to choose a form for ψ which allows strong correlation between the electrons. To that end I have experimented with simplified special cases of the function[12]

$$\psi = (1+bS)\exp(-\delta S)\cosh(\epsilon t)(1+Cu) \ , \qquad (8)$$

where $S=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$, and b, δ, ϵ, and C are the variational parameters. A virtue of the wave function in Eq. (8) is that $\chi(k)$ can be obtained analytically in terms of elementary functions by integrating over the Hylleraas coordinates s, t, and u. Correlation is provided by the factor $(1+Cu)$.

The two trial functions actually used in the computations reported here are obtained from Eq. (8) by setting either $\epsilon=0$, which is preferred for large α with $\alpha \gtrsim R$, or $b=0$, which is better for α sufficiently small compared to R.

In order to estimate the binding energy of the D^- center, that is, the minimum energy necessary to remove *one* of the electrons to infinity, leaving behind a neutral donor (D^0), it is necessary to subtract from $E^{(D^-)}$ the D^0 ground-state energy, $E^{(D^0)}$, and that of the free polaron. To this end I have calculated these energies also by means of the BP ansatz,[6] which, for $\alpha \leq 6$, gives $-\alpha$ for the free-polaron ground state. The electronic wave function for the donor is taken in the two-parameter form

$$(1+br)\exp(-Ar) \qquad (9)$$

[which gives a significant improvement over $\exp(-Ar)$, used previously,[6,13] when $\alpha > 1$ and $\alpha \gtrsim R$].

Calculated ratios of D^- to D^0 binding energies as functions of α are plotted in Fig. 1 for $R=1$ and 4. The horizontal line represents the "exact" theoretical ratio of 0.0555 for nonpolar crystals ($\alpha=0$), which is independent of the static dielectric constant or electron effective mass.

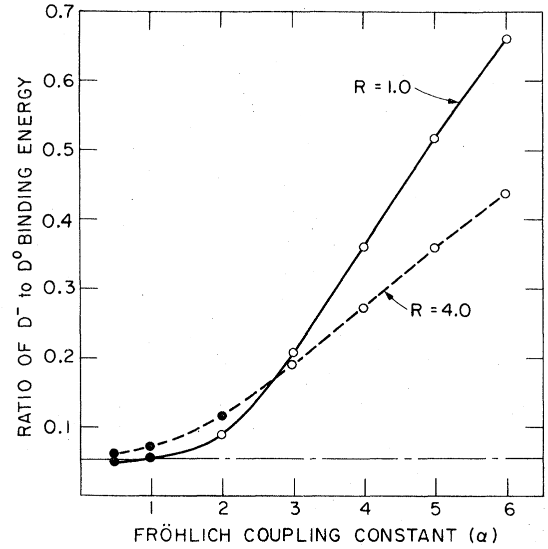

FIG. 1. Variation of the ratio of D^- to D^0 binding energy as a function of the Fröhlich coupling constant for two values of R. The solid circles were calculated using Eq. (8) with $b=0$, the open circles with $\epsilon=0$. (The trial function giving the lower energy is always employed.) The horizontal dashed line indicates the ratio 0.0555, correct for $\alpha=0$.

As α increases the (positive) static polarization charge near the center of the D^- ion increases, drawing in both electrons, but especially the outer electron. For $\alpha \gtrsim 2$ and $R=1$ the distinction between the outer and inner orbital disappears in the ansatz employed. As the electrons become more highly localized, the optimum value of the correlation parameter C in Eq. (8) grows in order to minimize the electrostatic repulsion between the polarons. Thus the D^- center goes from a weakly correlated, loosely bound state at small α to a compact, strongly correlated configuration at large α.

It is very likely, though not certain, that the D^- binding energies calculated here are smaller than the true D^- binding energies. Experimentation indicates, for example, that there is considerable room for improvement in Eq. (8) but much less so in Eq. (9).

Since the basic Hamiltonian H used in this work is

TABLE I. Results of calculations of the D^- and D^0 ground-state energies, $E_v^{(D^-)}$ and $E_v^{(D^0)}$, respectively. Binding energies are denoted E_B. All energies are in units of $\hbar\omega$ (= 124 and 197 cm^{-1} in AgBr and AgCl, respectively).

	α	R	$E_v^{(D^-)}$	$E_v^{(D^0)}$	$E_B^{(D^-)}$	$E_B^{(D^0)}$	$E_B^{(D^-)}/E_B^{(D^0)}$
AgBr	1.64	1.68	−5.637	−3.817	0.180	2.177	0.083
AgCl	1.9	1.9	−6.643	−4.482	0.261	2.582	0.101

based on a dielectric continuum-effective mass model, one does not expect that it would appropriately describe F' centers in the alkali halides. However, shallow donorlike centers, to which the model should apply, are known to exit in high-purity AgBr and AgCl.[13–16]

Energies calculated ignoring central cell effects for ground states of D^- and D^0 centers in AgBr and AgCl are presented in Table I. For AgBr D^- calculations, the $b=0$ version of Eq. (8) is employed, whereas $\epsilon=0$ is used for AgCl. Setting C equal to zero makes the D^- center unbound in the calculation.

The parameters α and R listed in Table I were calculated from data in Ref. 17 except $\hbar\omega$ is taken equal to 124 cm^{-1} in AgBr.[14] One obtains binding energies of 22 and 51 cm^{-1}, respectively, for D^- centers in AgBr and AgCl. These low-frequency regions have not yet, apparently, been explored experimentally.[13]

It is not possible at this time to estimate reliably from experiment the size of the central cell shift in the donorlike centers of the silver halides because the binding energy of the relevant $2p$ levels have not yet been calculated with sufficient accuracy. However, the central cell correction is believed to be *positive* (repulsive). Thus, the binding energies just quoted must be treated with caution since, as pointed out above, the binding enhancement is associated with a drawing-in of the orbit of the outer electron, and, therefore, the D^- binding energy is expected to be sensitive to central cell effects. The actual binding energies of D^- centers in the silver halides may, for this reason, be lower than my variational estimates.

The variational ansatz used here is expected to be least accurate for $\alpha < 1$ and $R < 1$, which is the region relevant to hydrogenic centers in the II–VI semiconductors. (In that range, the BPH ansatz of Ref. 6 would appear to be much more suitable.) Nevertheless, I have calculated D^- binding energies for various combinations of α and R relevant to II–VI semiconductors and find D^- binding energies near to but less than the value 0.052, which is the result obtained for $\alpha=0$ from the trial function of Eq. (8). This finding is consistent with magneto-optical data in CdS.[18]

Calculations presented above show how strongly the D^- photoionization threshold energy increases with α. It can be anticipated that the line profile will also be quite different at large α than at $\alpha=0$. When the coupling is strong the presence of a large amount of static polarization charge in the D^- center should give rise to intense multiphonon replicas superimposed on the zero-phonon photoionization line. A detailed calculation of the resulting line shape has not been attempted.

ACKNOWLEDGMENT

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