Dynamic Jahn-Teller Effect for a Double Acceptor or Acceptor-Bound Exciton in Semiconductors: Mechanism for an Inverted Level Ordering

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The dynamic Jahn-Teller effect provides a simple mechanism for inverting the ordering of the $J=0,2$ levels of the two equivalent holes in a neutral double acceptor or an exciton bound at a neutral acceptor. Whereas Hund's rule places the $J=2$ level below $J=0$, Jahn-Teller coupling to E and/or T_2 vibrational modes tends to shift $J=0$ below $J=2$, while splitting $J=2$ into its Γ_3 and Γ_5 components. Alternative proposed explanations involving central-cell, Stark, and strain effects fail to introduce the attractive interaction needed to offset the hole's Coulomb repulsion.

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Two extensively studied defects in semiconductors, the exciton bound to a neutral acceptor [1] and the neutral double acceptor [2], each contains two equivalent holes in $j=\frac{3}{2}$ single-hole states. The corresponding antisymmetric two-hole states have total angular momentum $J=0,2$, and Hund's rule predicts the $J=2$ levels to be more tightly bound than $J=0$ [3]. Yet an inverted ordering of these states has been confirmed for many of these defects; for example, for the double acceptors Zn and Be in Ge [2,4], and for bound excitons at the acceptors Al, Ga, and In in Si [1,5] and Sn in GaAs [6]. Despite several suggestions as to its origin [7,8], this inverted ordering has remained a puzzle for nearly twenty years. Overlooked in these discussions has been the fact that the Jahn-Teller (JT) coupling of the individual bound holes to E and T_2 vibrational modes has a form which *ensures* an inverted ordering, *via* a dynamic JT effect, if the JT coupling is strong enough to overcome the hole's Coulomb repulsion. The purpose of this paper is to demonstrate the likelihood that this inverted ordering arises in this way.

Well known since the work of Jahn and Teller [9] is the fact that coupling between electrons and asymmetric vibrational modes tends to remove *electronic* degeneracy (except for Kramers degeneracy) *via* a spontaneous distortion to lower symmetry. It is also well known that the JT effect does *not* lift the degeneracy of states of the coupled vibrational-electronic (vibronic) system that belong as partners to one of the irreducible representations (IR) of the original symmetry group, tending instead to replace electronic degeneracy by orientational degeneracy [10]. Less frequently encountered is the situation in which even a weak JT coupling can lift an *accidental* degeneracy of vibronic states belonging to *different* IR of the original group. This is the situation of the $J=0$ (Γ_1) and $J=2$ (Γ_3,Γ_5) states of the holes when their Coulomb interaction is ignored. A dynamic JT effect can therefore be expected not only to displace the $J=0$ and $J=2$ levels differently but also to split $J=2$ into its Γ_3 and Γ_5 components if the coupling to E and T_2 modes is not "isotropic." Just such a situation was encountered earlier in the "crystal-field" splitting of Γ_{3g} and Γ_{4g} components of the $J=2$ excited spin-orbit level of Fe^{2+} in MgO by a dynamic JT effect [11].

An individual bound hole in a Γ_8 ($j=\frac{3}{2}$) state at a tetrahedral site has linear JT coupling [12,13] with E modes Q_θ, Q_ε, and T_2 modes Q_ξ, Q_η, Q_ζ that can be expressed as

$$\mathcal{H}_{\rm JT}(h)=V_E(Z_\theta Q_\theta+Z_\varepsilon Q_\varepsilon)+V_T(Z_\xi Q_\xi+Z_\eta Q_\eta+Z_\zeta Q_\zeta)\,. \tag{1}$$

Here V_E (V_T) is the one-hole JT coupling coefficient for E (T_2) modes, and the operators $Z_\theta=j_Z^2-\frac{1}{3}j^2$, $Z_\varepsilon=(j_x^2-j_y^2)/\sqrt{3}$, $Z_\xi=(j_yj_z+j_zj_y)/\sqrt{3}$, etc., are given in terms of the components of hole angular momentum. We then form antisymmetric wave functions of Γ_1 ($J=0$) and Γ_3,Γ_5 ($J=2$) symmetry for two equivalent Γ_8 holes [14]. In this basis the JT coupling $\mathcal{H}_{\rm JT}(h_1)+\mathcal{H}_{\rm JT}(h_2)$ takes the form

$$\mathcal{H}_{\rm PJT}=2V_E(U_\theta Q_\theta+U_\varepsilon Q_\varepsilon)+2V_T(U_\xi Q_\xi+U_\eta Q_\eta+U_\zeta Q_\zeta)\,. \tag{2}$$

The only nonzero matrix element of U_i is that given by

$$\langle\Gamma_1|U_i|\Gamma_{ni}\rangle=1\,, \tag{3}$$

where $n=3$ for $i=\theta,\varepsilon$ and $n=5$ for $i=\xi$, η, or ζ. There is no coupling within the sets of states Γ_3 and Γ_5 or between Γ_3 and Γ_5; in the Γ_1,Γ_3,Γ_5 manifold the coupling to the Q's therefore represents a pure pseudo-JT coupling. The full vibronic Hamiltonian combines $\mathcal{H}_{\rm PJT}$ with harmonic oscillator Hamiltonians for each of the modes, for which $\mu_E,\mu_T,\omega_E,\omega_T$ denote effective masses and angular frequencies. We assume for simplicity that the Γ_1, Γ_3, and Γ_5 states are degenerate in the absence of JT cou-

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pling, thus omitting for the present the Coulomb interaction of the holes.

If V_E and V_T are small, we may use second-order perturbation theory to find the effect of the JT coupling on the lowest levels $|\Gamma_i 0\rangle$ of Γ_1, Γ_3, and Γ_5 symmetry, which in zero order are product states of the appropriate hole state $|\Gamma_i\rangle$ with the vibrational ground state with no quanta excited,

$$|\Gamma_i 0\rangle = |\Gamma_i\rangle |0_\theta 0_\varepsilon 0_\xi 0_\eta 0_\zeta\rangle . \tag{4}$$

The state $|\Gamma_1 0\rangle$ is coupled in first order by $\mathcal{H}_{\mathrm{PJT}}$ to each of five higher states; for example, to $|\Gamma_{5\zeta}\rangle |0_\theta 0_\varepsilon 0_\xi 0_\eta 1_\zeta\rangle$, in each of which one vibrational quantum is excited, so that the energy displacement of $|\Gamma_1 0\rangle$ is

$$\Delta E(\Gamma_1 0) = -4V_E^2/\mu_E\omega_E^2 - 6V_T^2/\mu_T\omega_T^2 . \tag{5}$$

Each of the states $|\Gamma_{3i} 0\rangle$ and $|\Gamma_{5i} 0\rangle$ is coupled to a single higher state, yielding

$$\begin{aligned} \Delta E(\Gamma_3 0) &= -2V_E^2/\mu_E\omega_E^2 , \\ \Delta E(\Gamma_5 0) &= -2V_T^2/\mu_T\omega_T^2 . \end{aligned} \tag{6}$$

The degeneracy of $|\Gamma_3 0\rangle$ and $|\Gamma_5 0\rangle$ is therefore lifted by $\mathcal{H}_{\mathrm{PJT}}$ if $|V_E| \neq |V_T|$, but $|\Gamma_1 0\rangle$ is displaced the most and then always becomes the lowest level.

For stronger coupling, we remark that if coupling is only with T_2 modes the Γ_3 states are unaffected and that the vibronic problem of the Γ_1 and Γ_5 states is then mathematically identical to that of the relaxed excited state of the F center [15], in which $s(\Gamma_1^+)$ and $p(\Gamma_4^-)$ electronic states are coupled by a Γ_4^- mode. A full analysis of the latter problem shows that an s-like vibronic state is displaced below the lowest p-like state as the coupling strength increases, whatever the initial ordering of the electronic states [15]. From this work one finds for strong coupling that the separation of the states $|\Gamma_1 0\rangle$ and $|\Gamma_5 0\rangle$ of our present problem is given by

$$E(\Gamma_5 0) - E(\Gamma_1 0) = \tfrac{1}{2}\hbar\omega_T(\hbar\omega_T/E_T) , \tag{7}$$

where $E_T = 2V_T^2/\mu_T\omega_T^2$ is the analog of a JT energy. The corresponding analysis [16] of the pure pseudo-JT case for $\Gamma_1 + \Gamma_3$ similarly yields

$$E(\Gamma_3 0) - E(\Gamma_1 0) = \tfrac{1}{4}\hbar\omega_E(\hbar\omega_E/E_E) , \tag{8}$$

with E_E given by $2V_E^2/\mu_E\omega_E^2$. For cases involving coupling to both E and T_2 modes the analysis is more difficult, but an argument based on the fact that for strong coupling the Berry phase is zero in the adiabatic ground state indicates that Γ_1 is then always the lowest level [17].

Experimental values of the energy differences between the two-hole Γ_1, Γ_3, and Γ_5 states are in the range of a few meV or less for double acceptors and acceptor-bound excitons in Si, Ge, and the III-V compounds [1,2]. For example, for the bound exciton at Si:Ga, Γ_1 lies below Γ_5 by 1.45 ± 0.05 meV, and Γ_3 is above Γ_5 by 0.32 ± 0.03 meV [5]. For the double acceptor Ge:Zn, Γ_1 is the lowest level by 2.4 ± 0.1 meV [4]. Splittings of this size would be consistent with a weak JT coupling, for which a perturbation treatment as in Eqs. (5) and (6) may suffice and would then yield

$$\begin{aligned} [E(\Gamma_3 0) + E(\Gamma_5 0)]/2 - E(\Gamma_1 0) \\ = 3V_E^2/\mu_E\omega_E^2 + 5V_T^2/\mu_T\omega_T^2 - E_C . \end{aligned} \tag{9}$$

Here E_C is a positive energy representing the Coulomb splitting between the $J=2$ level and the higher $J=0$ level when JT coupling is ignored. Alternatively, such results could also be consistent with strong JT coupling and expressions such as Eqs. (7) and (8) if we had $E_T \gg \hbar\omega_T$ or $E_E \gg \hbar\omega_E$ and $\hbar\omega_T$ or $\hbar\omega_E$ moderately large, say 10 meV or more. This latter possibility can be ruled out, however, because it would imply a contribution of the order of the larger of E_E or E_T to the binding energy of the two holes at the defect. Since the JT energy of a single hole in a Γ_8 state coupled as in Eq. (1) (or that of three bound holes, which also have a Γ_8 collective ground state) should only be about one-quarter as much, a large increase (decrease) in binding should occur in going from one (two) to two (three) holes at the defect. No such variation in binding energies is known to occur, aside from that given for the second hole by the extra binding of the Γ_1 level relative to Γ_3 and Γ_5 [1,2,18].

Assuming a weak JT coupling for the holes so that Eqs. (5), (6), and (9) are valid, we may ask if it is plausible that this coupling is strong enough to account for an inverted level splitting in the meV range observed. We first consider a shallow bound hole as described by effective-mass theory (EMT). For appreciable coupling phonons must have wave vectors lying near the center of the Brillouin zone, since only these produce a more or less uniform deformation extending across the hole orbit and thus split the hole's Γ_8 ground state via the deformation-potential coupling to the strain. Approximating the hole ground state as having a radial dependence $\propto \exp(-r/a^*)$, we may obtain the energy shifts of the Γ_1, Γ_3, and Γ_5 states of two equivalent holes by treating the deformation-potential coupling to acoustic phonons in second-order perturbation theory, as in Eqs. (5) and (6). We obtain in this way [16]

$$\begin{aligned} \Delta E(\Gamma_1 0)/(6b'^2 + 3d'^2) = \Delta E(\Gamma_3 0)/3b'^2 = \Delta E(\Gamma_5 0)/d'^2 \\ = -[1 + (2s_T^2/3s_L^2)]/40\pi\rho a^{*3} s_T^2 . \end{aligned} \tag{10}$$

Here ρ is the density of the crystal, s_T and s_L are sound velocities in the transverse and longitudinal branches, and b' and d' are deformation potentials for a bound hole. Taking as representative of acceptors in Si the values $b' = -1.61$ eV, $d' = -4.50$ eV measured [19,20] for Si:B, we find we would need a value $a^* = 9.8$ Å in Eq. (10) in order to account for the 1.45 meV separation of the Γ_1 and Γ_5 states of the bound exciton at Si:Ga. A nonzero

Coulomb contribution E_C to this separation, as in Eq. (9), would require an even smaller value for a^*. Since such a value for a^* is already much smaller than the value 25.5 Å obtained theoretically with EMT by Baldareschi and Lipari [21] for a hole bound in Si by a single Coulomb charge ($Z=1$), we conclude that in Si a hole as described in EMT does not have sufficient coupling to acoustic phonons to explain the observed splitting of the bound-exciton states. In Ge the situation is even less promising because of the greater spatial extent of the bound holes.

All acceptors that have been found to have the inverted level structure bind a hole more strongly than given by EMT, however, and this increased binding has the effect of reducing the extent of the wave function and thus the value of a^* that should be used in Eq. (10). This reduction of a^* increases the splittings predicted by Eq. (10), though probably not by enough to agree with the observed splitting, particularly if a nonzero Coulomb splitting E_C must also be offset. But in addition to enhancing the effect of coupling to long-wavelength acoustic modes, the localized potential responsible for the increased binding may cause the holes to be weakly coupled to localized vibrations corresponding to linear combinations of phonons with wave vectors extending as far as the surface of the Brillouin zone. Using such a coupling together with Eqs. (5) and (6), we could account for the Γ_1 level being displaced by, say, 2 meV relative to the Γ_3 and Γ_5 levels if E_T and E_E had values ~ 0.5 meV, a quite plausible value compared to JT energies that can easily be in the range 0.1 eV to 1.0 eV for centers in semiconductors that are localized on an atomic scale [22]. We suggest, therefore, that the inverted level ordering is evidence that JT coupling to such short-wavelength vibrational modes is present for these centers.

A number of other mechanisms [7,8], including electronic correlation, central-cell corrections, and Stark and strain effects, have been proposed as possible explanations for the inverted ordering. However, none of these other effects changes the fact that the Coulomb interaction between the holes is repulsive, while the inverted ordering requires an attractive net interaction. In particular, central-cell corrections and the proposed Stark and strain effects affect the holes independently without changing the Γ_8 symmetry of the single-hole wave functions. Determinantal wave functions formed from such Γ_8 states for two equivalent holes necessarily yield a higher energy for the Γ_1 state than for either Γ_3 or Γ_5 if the mutual interaction of the holes is repulsive [16]. A suggestion has been made by Giesekus and Falicov [23] that the Coulomb repulsion of the holes may somehow be overcompensated in the case of a double acceptor by dynamic many-body effects, perhaps involving a rearrangement of the lattice when two holes are nearby. The JT effect offers a specific realization of this suggestion, in that placing two holes in the same orbital (with opposing spins) tends to maximize the energy gained from the lattice relaxation resulting from the JT coupling. The JT coupling thus tends to draw the two holes into the same region of space, in contrast to the Coulomb interaction that tries to keep them apart. The effect is identical with that of the JT coupling in systems [24] with a "negative U" and recalls the role played by phonons in pairing electrons in the BCS theory of superconductivity.

The problem of the dynamic JT effect for an electronic Γ_8 state was first considered by Moffitt and Thorson [12]; the possible importance of the dynamic JT effect in affecting the properties of individual holes in semiconductors, particularly holes bound more deeply than given by EMT, was later noted by Morgan [13]. Shallow acceptor centers have indeed been shown to be strong scattering centers for acoustic phonons because of their JT coupling [25], but the reciprocal effect of this coupling on the states of a shallow hole is small because of the large spatial extent of the hole wave functions. Since large hole orbits limit the effective coupling to long-wavelength phonons, JT energies are very small even when deformation potentials are large, a result found also for shallow donors [26]. The importance of the JT coupling for the centers considered in the present work must reflect the fact that the holes in these centers are deeper than given by EMT and thus are more susceptible to effects of local vibrations.

It has been suggested by Kaufmann *et al.* [27] that a dynamic JT effect may affect the levels of the double acceptor Si:Zn, but no specific model was cited nor was any connection noted to a possible inversion of the levels. Earlier, a static JT effect was proposed by Moore [28] as a mechanism for lowering the site symmetry of a double acceptor and thus adding structure in its optical spectra, and Averkiev *et al.* [29] have studied the adiabatic energy surfaces corresponding to the static JT problem of two holes. Neither of these treatments considered a dynamic JT effect. We emphasize that in the centers considered in the present work the JT energies appear to be at most a few meV, much too small to cause a static JT effect, for which one must have a JT energy large compared to $\hbar\omega$ of all the effective modes [10].

In summary, we have shown that a dynamic JT effect tends to displace the $J=0$ (Γ_1) level of two equivalent bound holes below the $J=2$ (Γ_3,Γ_5) levels, while separating the latter. Of the various mechanisms that have so far been suggested to explain this inverted ordering, only the JT coupling introduces the needed attractive interaction between the holes. Although holes as described by EMT are too weakly coupled to lattice phonons to account for the observed splitting, we argue that it is likely that JT coupling of the strength required involves vibrations of shorter wavelength to which the coupling is enhanced because the holes are deeper than given by EMT.

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[1] M. L. W. Thewalt, in *Excitons*, edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), p. 393.
[2] M. L. W. Thewalt, D. Larie, I. J. Booth, B. P. Clayman, E. C. Lightowlers, and E. E. Haller, Physica (Amsterdam) **146B**, 47 (1987).
[3] R. A. Chapman, W. G. Hutchinson, and T. L. Estle, Phys. Rev. Lett. **17**, 132 (1966).
[4] M. L. W. Thewalt, B. P. Clayman, and D. Labrie, Phys. Rev. B **32**, 2663 (1985); D. Labrie, I. J. Booth, M. L. W. Thewalt, and E. E. Haller, Phys. Rev. B **38**, 5504 (1988).
[5] M. L. W. Thewalt, Phys. Rev. Lett. **38**, 521 (1977); K. R. Elliott, G. C. Osbourne, D. L. Smith, and T. C. McGill, Phys. Rev. B **17**, 1808 (1978); S. A. Lyon, D. L. Smith, and T. C. McGill, Phys. Rev. B **17**, 2620 (1978).
[6] W. Schairer, D. Bimberg, W. Kottler, K. Cho, and M. Schmidt, Phys. Rev. B **13**, 3452 (1976).
[7] D. C. Herbert, J. Phys. C **10**, 3327 (1977).
[8] T. N. Morgan, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors*, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 391.
[9] H. A. Jahn and E. Teller, Proc. R. Soc. London A **161**, 220 (1937).
[10] F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972), p. 1.
[11] F. S. Ham, W. M. Schwarz, and M. C. M. O'Brien, Phys. Rev. **185**, 548 (1969); see Fig. 1.
[12] W. Moffitt and W. Thorson, Phys. Rev. **108**, 1251 (1957).
[13] T. N. Morgan, Phys. Rev. Lett. **24**, 887 (1970).
[14] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, MA, 1963), p. 98.
[15] F. S. Ham, Phys. Rev. B **8**, 2926 (1973).
[16] C. H. Leung and F. S. Ham (to be published).
[17] F. S. Ham, J. Phys. Condens. Matter **2**, 1163 (1990).
[18] For weak coupling the additional vibronic binding for a Γ_8 hole (or for three holes) in the same approximation as in Eqs. (5) and (6) is $E(\Gamma_8 0) = -V_E^2/\mu_E\omega_E^2 - V_T^2/\mu_T\omega_T^2$. If the coupling were roughly isotropic, $|V_E| \sim |V_T|$, this would then be much the same as for the Γ_3 and Γ_5 levels for two holes as given by Eq. (6), and only the Γ_1 level for two holes should exhibit extra binding due to the JT coupling. (We assume that the values of V_E and V_T are roughly independent of the number of bound holes.)
[19] H. R. Chandrasekar, P. Fisher, A. K. Ramdas, and S. Rodriguez, Phys. Rev. B **8**, 3836 (1973).
[20] The measured values of b' and d' for the more deeply bound acceptors Al, Ga, and In (Ref. [19]) are somewhat smaller than for B. However, a dynamic JT effect in the Γ_8 ground state of a hole partially quenches both b' and d' (Ref. [13]), and it is the unreduced values we should use in Eq. (10). For this reason we take the values for Si:B in our calculation.
[21] A. Baldareschi and N. O. Lipari, Phys. Rev. B **8**, 2697 (1973).
[22] G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 147.
[23] A. Giesekus and L. M. Falicov, Phys. Rev. B **42**, 8975 (1990).
[24] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 5662 (1980).
[25] J. Maier and E. Sigmund, Phys. Rev. B **34**, 5562 (1986).
[26] G. D. Watkins and F. S. Ham, Phys. Rev. B **1**, 4071 (1970).
[27] B. Kaufmann, A. Dörnen, M. Lane, G. Pensl, D. Grünebaum, and N. Stolwijk, Mater. Sci. Forum **83-87**, 197 (1992).
[28] W. J. Moore, Phys. Rev. B **29**, 7062 (1984).
[29] N. S. Averkiev, A. A. Gutkin, E. B. Osipiv, and V. E. Sedov, Fiz. Tekh. Poluprovodn. **21**, 415 (1987) [Sov. Phys. Semicond. **21**, 258 (1987)].