¹N. Friedman, Bull. Am. Phys. Soc. **16**, 123 (1971). A similar problem, in which only the EDP interaction was considered, has long been of interest in the case of metals. This study was initiated by S. Koshino, Prog. Theor. Phys. **24**, 484 (1960); a recent paper by S. Takeno [Prog. Theor. Phys. **42**, 1003 (1969)] gives references to previous work. A difficulty in these papers is that the rigid-ion EDP interaction employed can be shown to give negligible results when treated exactly; see P. L. Taylor, Proc. Phys. Soc. Lond. **80**, 755 (1962). A work which considers EP-ED effects (but ignores the EDP interaction) is D. L. Mills, Phys. Rev. Lett. **26**, 242 (1971), but this employs a defective scheme of calculation, as shown in the Appendix here. D. A. Smith, J. Phys. C **4**, L145 (1971) also pointed out defects in Mills's calculation.

²The effective absence of electron statistics permits us to use a simpler formalism than is usual. We follow the formulation of G. Rickayzen, in *Lecture Notes on the Many Body Problem* (Bergen International School of Physics, New York, 1962), p. 85.

³See Rickayzen (Ref. 2).

⁴This is why the superconducting state cannot be generated from a gas of free electrons by perturbation theory, and the result usually appears in that form. However, note C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), p.7, Eq. (45), in which it appears that the perturbation treatment fails entirely in case the exact ground state is orthogonal to the unperturbed ground state. Should the two differ in symmetry, they would be orthogonal.

⁵H. Y. Fan, Phys. Rev. **82**, 900 (1951).

⁶G. D. Whitfield, Phys. Rev. 121, 720 (1961).

 7 This argument is based on a private communication by R. Brout.

⁸We follow the derivation of second-order theory by P. A. M. Dirac [*Principles of Quantum Mechanics*, 4th ed. (Oxford U. P., Oxford, England, 1958), p. 178].

⁹Such a solution is proposed by Mills; see Ref 1.

PHYSICAL REVIEW B

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Ground-State Energy of a Wannier Exciton in a Polar Crystal

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An analytic expression for the ground-state energy of a Wannier exciton, interacting with the longitudinal-optical-phonon field of the crystal lattice, is derived. The coupling between the constituents of the exciton, i.e., the electron and the hole, and the optical-phonon field is assumed to be weak, and hence second-order perturbation theory as formulated by Dalgarno and Lewis is used. The theoretically calculated value of the ground-state energy is then compared with its experimentally determined values in various polar crystals and a good agreement is found.

INTRODUCTION

In recent years there has been a great deal of interest in both the theoretical and experimental investigations of the energy spectrum of a Wannier exciton in polar crystals.¹⁻¹⁴ Haken,^{1,2} for instance, has calculated an effective potential between a hole and an electron in a polar crystal using the variational wave functions of Lee, Low, and Pines.¹⁵ Because of the nature of the approximations made in his calculations, the potential he derives is valid only when the Bohr radius of the exciton is much larger than the extensions of the electron and the hole polarons. Recently Mahanti and Varma⁵ have suggested an interpolation scheme to calculate the ground-state energy (E_{R}) of a Wannier exciton in a polar crystal using a method based on the many-body approach of Sham and Rice.¹⁶ Their method, however, involves rather complicated numerical computations. The binding energy of excitons has recently been measured in a number of polar crystals.⁷⁻¹⁴ Bachrach and Brown,¹⁰ for instance, have determined this quantity experimentally in the case of thallium bromide and thallium chloride. They found that the use of the simple hydrogenic formula gave values for the binding

energy which did not agree with the experimental values at all. Assuming a hydrogenic trial wave function, they also calculated the binding energies variationally using Haken's^{1,2} potential and found that these values differed from the experimental values by orders of magnitude in the case of thal-lium halides.

In this paper we derive an analytic expression for the ground-state energy of a Wannier exciton in a polar crystal. We assume that the coupling between the constituents of the exciton, i.e., the electron, the hole, and the longitudinal-opticalphonon field, is weak and hence use second-order perturbation theory as formulated by Dalgarno and Lewis.¹⁷ We then compare the value of the groundstate energy thus calculated with its experimentally determined values in various polar crystals. As shown in Table II, there is a good agreement between the theoretical and the experimental values.

THEORY

Our system consists of a conduction electron and a hole, coupled together by an attractive screened-Coulomb potential, and both interacting with the longitudinal-optical-phonon field of the crystal lattice. The Hamiltonian of this system is given by

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{e^2}{\epsilon_{\infty} |\vec{r}_1 - \vec{r}_2|} + \sum_{\vec{q}} \hbar \omega a_{\vec{q}}^{\dagger} a_{\vec{q}}$$
$$- \frac{U}{V^{1/2}} \sum_{\vec{q}} \frac{i}{q} (a_{\vec{q}} e^{i\vec{q} \cdot \vec{r}_1} - a_{\vec{q}}^{\dagger} e^{-i\vec{q} \cdot \vec{r}_1})$$
$$+ \frac{U}{V^{1/2}} \sum_{\vec{q}} \frac{i}{q} (a_{\vec{q}} e^{i\vec{q} \cdot \vec{r}_2} - a_{\vec{q}}^{\dagger} e^{-i\vec{q} \cdot \vec{r}_2}), \quad (1)$$

where \vec{p}_1 , m_1 , and \vec{r}_1 are the momentum, band mass, and position coordinate of the electron, and \vec{p}_2 , m_2 , and \vec{r}_2 refer to similar parameters for the hole. The creation and annihilation operators for an optical phonon of wave vector \vec{q} are designated by $a_{\vec{q}}^{\dagger}$ and $a_{\vec{q}}$, respectively. The opticalphonon frequency ω is assumed to be independent of \vec{q} . The parameter U is defined as

$$U = \hbar \omega (4\pi \alpha_i)^{1/2} (\hbar/2m_i \omega)^{1/4} , \qquad (2)$$

where α_i (for i=1, 2) is the dimensionless coupling constant first introduced by Fröhlich¹⁸ and is defined as

$$\alpha_{i} = \frac{e^{2}}{\hbar} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_{0}} \right) \left(\frac{m_{i}}{2\hbar\omega} \right)^{1/2} \,. \tag{3}$$

The quantity U is independent of the mass and is therefore the same for the electron and the hole. Here ϵ_0 and ϵ_{∞} are the static and the high-frequency dielectric constants, respectively, and V is the volume of the crystal.

Making the following transformation to the center-of-mass (\vec{R}) and the relative (\vec{r}) coordinates

$$\vec{\mathbf{r}}_1 = \mathbf{\hat{R}} + (m_2/M)\mathbf{\hat{r}} , \qquad (4a)$$

$$\vec{\mathbf{r}}_2 = \vec{\mathbf{R}} - (m_1/M)\vec{\mathbf{r}} , \qquad (4b)$$

where $M = m_1 + m_2$, we obtain

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} - \frac{e^2}{\epsilon_{\infty}r} + \sum_{\bar{\mathfrak{q}}} \bar{\hbar}\omega a_{\bar{\mathfrak{q}}}^{\dagger} a_{\bar{\mathfrak{q}}}$$
$$- \frac{U}{V^{1/2}} \sum_{\bar{\mathfrak{q}}} \frac{i}{q} \left(a_{\bar{\mathfrak{q}}} e^{i\bar{\mathfrak{q}} \cdot [\vec{\mathfrak{R}} + (m_2/M)\vec{\mathfrak{r}}]} - a_{\bar{\mathfrak{q}}}^{\dagger} e^{-i\bar{\mathfrak{q}} \cdot [\vec{\mathfrak{R}} + (m_2/M)\vec{\mathfrak{r}}]} \right)$$
$$+ \frac{U}{V^{1/2}} \sum_{\bar{\mathfrak{q}}} \frac{i}{q} \left(a_{\bar{\mathfrak{q}}} e^{i\bar{\mathfrak{q}} \cdot [\vec{\mathfrak{R}} - (m_1/M)\vec{\mathfrak{r}}]} - a_{\bar{\mathfrak{q}}}^{\dagger} e^{-i\bar{\mathfrak{q}} \cdot [\vec{\mathfrak{R}} - (m_1/M)\vec{\mathfrak{r}}]} \right).$$
(5)

In the above expression \vec{P} is the center-of-mass momentum, \vec{p} is the relative momentum, and μ is the reduced mass, i.e.,

$$1/\mu = 1/m_1 + 1/m_2$$
.

To eliminate the center-of-mass-dependent terms from Eq. (5), we use the following canonical trans-

formation. Define

 $\mathcal{K} = e^{is} H e^{-is}$, where

$$s = (1/\hbar) \left(\vec{\mathbf{K}} - \sum_{\vec{\mathbf{q}}} \hbar \vec{\mathbf{q}} a_{\vec{\mathbf{q}}}^{\dagger} a_{\vec{\mathbf{q}}} \right) \cdot \vec{\mathbf{R}}$$
(7)

and

$$\vec{\mathbf{K}} = \vec{\mathbf{P}} + \sum_{\vec{a}} \hbar \vec{\mathbf{q}} a_{\vec{a}}^{\dagger} a_{\vec{a}} .$$
(8)

Here \tilde{K} is a constant of the motion, i.e.,

$$[H, \vec{\mathbf{K}}] = \mathbf{0} \ . \tag{9}$$

The transformed Hamiltonian can then be written

$$\mathcal{H} = H_0 + H_1 + H_2 + H_3 + H_4 , \qquad (10)$$

where

$$H_0 = \frac{p^2}{2\mu} - \frac{e^2}{\epsilon_{\infty} r} \quad , \tag{11}$$

$$H_1 = \sum_{\mathbf{d}} \hbar \omega a_{\mathbf{d}}^{\dagger} a_{\mathbf{d}} , \qquad (12)$$

$$H_{2} = -\frac{U}{V^{1/2}} \sum_{\vec{q}} \frac{i}{q} \left(a_{\vec{q}} e^{i (m_{2}/M)\vec{q} \cdot \vec{r}} - a_{\vec{q}}^{\dagger} e^{-i (m_{2}/M)\vec{q} \cdot \vec{r}} \right),$$
(13)

$$H_{3} = \frac{U}{V^{1/2}} \sum_{\vec{q}} \frac{i}{q} \left(a_{\vec{q}} e^{-i(m_{1}/M)\vec{q}\cdot\vec{r}} - a_{\vec{q}}^{\dagger} e^{i(m_{1}/M)\vec{q}\cdot\vec{r}} \right),$$
(14)

$$H_4 = (1/2M) \left(\vec{\mathbf{K}} - \sum_{\mathbf{q}} \hbar \vec{\mathbf{q}} \, a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}} \right)^2 \,. \tag{15}$$

We are essentially interested in calculating the binding energy (which we also call ground-state energy with an opposite sign), which is given as the difference in energy between the states of the exciton corresponding to $n = \infty$ and n = 1. We therefore expect that H_4 will not make a significant contribution to this quantity and hence drop it from Eq. (10).

We now assume that both α_1 and α_2 are small and therefore calculate the ground-state energy of our system described by Eq. (10) using second-order perturbation theory. Treating $(H_0 + H_1)$ as an unperturbed Hamiltonian and $(H_2 + H_3)$ as a perturbation, we obtain for the shift in energy ΔE of the ground state at temperature T = 0°K

$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 , \qquad (16)$$

where

$$\Delta E_{1} = \frac{U^{2}}{V} \sum_{n} \sum_{\mathbf{\tilde{q}}} \frac{\langle i | e^{i (m_{2}/M)\mathbf{\tilde{q}} \cdot \mathbf{\tilde{r}}} | n \rangle \langle n | e^{-i (m_{2}/M)\mathbf{\tilde{q}} \cdot \mathbf{\tilde{r}}} | i \rangle}{q^{2}(E_{i} - E_{n} - \hbar\omega)} ,$$
(17)

$$\Delta E_2 = \frac{U^2}{V} \sum_n \sum_{\mathfrak{q}} \frac{\langle i | e^{-i (\mathfrak{m}_1/M) \mathfrak{q} \cdot \mathfrak{r}} | n \rangle \langle n | e^{i (\mathfrak{m}_1/M) \mathfrak{q} \cdot \mathfrak{r}} | n \rangle}{q^2 (E_i - E_n - \hbar \omega)} ,$$
(18)

$$\Delta E_{3} = -\frac{U^{2}}{V} \sum_{n} \sum_{\vec{q}} \frac{\langle i | e^{-i (m_{1}/M)\vec{q} \cdot \vec{r}} | n \rangle \langle n | e^{-i (m_{2}/M)\vec{q} \cdot \vec{r}} | i \rangle}{q^{2}(E_{i} - E_{n} - \hbar\omega)}$$
(19)

1473

(6)

1474

$$\Delta E_4 = \frac{-U^2}{V} \sum_{n} \sum_{\mathfrak{q}} \frac{\langle i | e^{i (m_2/M)\mathfrak{q} \cdot \mathbf{r}^{\dagger}} | n \rangle \langle n | e^{i (m_1/M)\mathfrak{q} \cdot \mathbf{r}^{\dagger}} | i \rangle}{q^2 (E_i - E_n - \hbar \omega)}$$
(20)

In these expressions $|i\rangle$ and E_i designate the eigenfunction and the eigenvalue of the ground state and $|n\rangle$ and E_n stand for the eigenfunction and the eigenvalue of the intermediate states. The summation here is over all the states of both positive and negative energies. The summation over n, however, is very difficult to perform and therefore an exact analytic evaluation of ΔE_1 , etc., in the forms given above is almost impossible. It is, however, possible to eliminate the summation over the intermediate states by modifying the above expressions using the following method. This method was first suggested by Dalgarno and Lewis¹⁷ to deal with problems involving second-order perturbation corrections to the hydrogenic systems. To evaluate ΔE_1 , for instance, we define an operator F_1 such that

$$\left(\left[F_{1}, H_{0}\right] - \hbar\omega F_{1}\right)\left|i\right\rangle = e^{-i\left(m_{2}/M\right)\vec{\mathfrak{q}}\cdot\vec{\mathfrak{r}}}\left|i\right\rangle.$$

$$(21)$$

Equation (17) then becomes

$$\Delta E_{1} = \frac{U^{2}}{V} \sum_{n} \sum_{\mathfrak{q}} \frac{\langle i | e^{i \langle m_{2} / M \rangle \mathfrak{q}^{\ast} \cdot \mathfrak{r}^{\ast}} | n \rangle \langle n | F_{1} H_{0} - H_{0} F_{1} - \hbar \omega F_{1} | i \rangle}{q^{2} (E_{i} - E_{n} - \hbar \omega)}$$
$$= \frac{U^{2}}{V} \sum_{\mathfrak{q}} \frac{1}{q^{2}} \langle i | e^{i \langle m_{2} / M \rangle \mathfrak{q}^{\ast} \cdot \mathfrak{r}} F_{1} | i \rangle .$$
(22)

Thus the summation over *n* is eliminated and we are left with an integral over the space coordinates and a summation over the phonon wave vectors. We can now evaluate ΔE_1 provided we can obtain an explicit form of the operator F_1 . Assuming with Dalgarno and Lewis that the operator F_1 is a function of space coordinates only and substituting explicitly for the ground-state wave function, i.e., $|i\rangle = (1/\pi a^3)^{1/2} e^{-r/a}$ in Eq. (21), we obtain

$$\nabla^2 F_1 - \frac{2}{a} \frac{\partial F_1}{\partial r} - \frac{2\mu\omega}{\hbar} F_1 = \frac{2\mu}{\hbar^2} e^{-i(m_2/M)\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}}, \quad (23)$$

where

$$a = \epsilon_{\infty} \hbar^2 / \mu e^2$$
 .

To obtain a solution of this inhomogeneous partial differential equation in an analytic form does not seem possible. However, if we insert complete sets of plane-wave states in the expression for ΔE_1 , we obtain

$$\Delta E_{1} = \frac{U^{2}}{V} \sum_{\mathbf{\tilde{q}}} \frac{1}{q^{2}} \sum_{\vec{\mathbf{k}}, \vec{\mathbf{k}}_{1}, \vec{\mathbf{k}}_{2}} \left(\left\langle i \middle| \vec{\mathbf{k}} \right\rangle \left\langle \vec{\mathbf{k}} \middle| e^{i \left(m_{2} / M \right) \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} \middle| \vec{\mathbf{k}}_{1} \right\rangle \right. \\ \left. \times \left\langle \vec{\mathbf{k}}_{1} \middle| F_{1} \middle| \vec{\mathbf{k}}_{2} \right\rangle \left\langle \vec{\mathbf{k}}_{2} \middle| i \right\rangle \right) .$$
(24)

Thus to evaluate ΔE_1 we need the matrix elements of F_1 between plane-wave states, and these are obtained from Eq. (21). Taking into account the assumption concerning the space dependence of the operator F_1 , we obtain for these matrix elements

$$\langle \vec{\mathbf{k}}_{1} | F_{1} | \vec{\mathbf{k}}_{2} \rangle = \frac{2\mu}{\hbar} \frac{\langle \vec{\mathbf{k}}_{1} | e^{-i(m_{2}/M)\vec{\mathbf{t}} \cdot \vec{\mathbf{r}}} | \vec{\mathbf{k}}_{2} \rangle}{k_{2}^{2} - k_{1}^{2} - 2\mu\omega/\hbar} \quad .$$
(25)

Substituting this expression in Eq. (24), transforming the summations to integrations by the usual methods, and using the orthogonality property of the plane-wave states, we obtain

$$\Delta E_1 = -\frac{2m_1 U^2}{\hbar^2 V} \sum_{\vec{\mathfrak{q}}} \sum_{\vec{\mathfrak{k}}} \frac{\langle i | \vec{\mathfrak{k}} \rangle \langle \vec{\mathfrak{k}} | i \rangle}{q^2 [(m_2/M)q^2 - 2\vec{\mathfrak{q}} \cdot \vec{\mathfrak{k}} + 2m_1 \omega/\hbar]}.$$
(26)

To evaluate ΔE_2 , ΔE_3 , and ΔE_4 , we define operators F_2 , F_3 , and F_4 , respectively, each one of them satisfying an equation completely analogous to Eq. (21). Assuming again that each of these operators is a function of space coordinates only, and carrying out similar calculations as in the case of ΔE_1 , we obtain

$$\Delta E_2 = -\frac{2m_2U^2}{\hbar^2 V} \sum_{\vec{k}} \sum_{\vec{k}} \frac{\langle i | \vec{k} \rangle \langle \vec{k} | i \rangle}{q^2 [(m_1/M)q^2 + 2\vec{q} \cdot \vec{k} + 2m_2\omega/\hbar]} \quad , \tag{27}$$

$$\Delta E_3 = -\frac{2m_1 U^2}{\hbar^2 V} \sum_{\mathbf{\tilde{q}}} \sum_{\mathbf{\tilde{k}}} \frac{\langle i | \mathbf{\tilde{k}} \rangle \langle \mathbf{\tilde{k}} + \mathbf{\tilde{q}} | i \rangle}{q^2 \{ [(m_2 + 2m_1)/M] q^2 + 2\mathbf{\tilde{q}} \cdot \mathbf{\tilde{k}} - 2m_1 \omega/\hbar \}} \quad , \tag{28}$$

$$\Delta E_4 = -\frac{2m_2U^2}{\hbar^2 V} \sum_{\vec{q}} \sum_{\vec{k}} \frac{\langle i | \vec{k} \rangle \langle \vec{k} - \vec{q} | i \rangle}{q^2 \{ [(m_1 + 2m_2)/M] q^2 - 2\vec{q} \cdot \vec{k} - 2m_2\omega/\hbar \}} .$$
⁽²⁹⁾

The evaluation of these various contributions to ΔE is described briefly in the Appendix. We obtain

$$\Delta E_1 = -\frac{8}{3} \alpha_1 \hbar \omega \, \frac{a}{\beta} \left(\frac{M}{m_2}\right)^{1/2} P_2 \left(\frac{1 + a^2/2\beta^2}{(1 + a^2/\beta^2)^{1/2}}\right) \quad , \tag{30}$$

where P_2 is a Legendre function of order two and

$$\begin{split} \Delta E_3 &= -\frac{\gamma_1 \pi^2}{2(2\pi)^4 b(\delta_1^2 - 2)} \left(\frac{1}{8b^3 (D_1^2 + 2bE_1 - b^2)} - \frac{b - E_1}{2b^2 (D_1^2 + 2bE_1 - b^2)^2} + \frac{E_1 + (X_1)^{1/2}}{X_1^{1/2} (E_1 + X_1^{1/2} + b) \left[(E_1 + X_1^{1/2})^2 - b^2 \right]^2} \right) \\ &+ \frac{\gamma_1 \pi^2}{(2\pi)^4} \left[-\frac{2}{\beta_1^6} \ln \left(\frac{Y_1^{1/2}}{b} \right) + \frac{1}{b^2 \beta_1^4} - \frac{1}{2b^2 \beta_1^2 Y_1} \right] + \frac{\gamma_1}{(2\pi)^4} \left\{ -\frac{2\pi^2}{\beta_1^6} \ln \left[\frac{b + Y_1^{1/2}}{2b} \left(\frac{(Y_1^{1/2} + E_1 + X_1^{1/2})(b - E_1 + X_1^{1/2})}{(b + E_1 + X_1^{1/2}) (Y_1^{1/2} - E_1 + X_1^{1/2})} \right)^{1/2} \right] \end{split}$$

$$+\frac{\pi^{2}}{2\beta_{1}^{4}}\left(\frac{1}{2b^{2}}+\frac{1}{Y_{1}^{1/2}(b+Y_{1}^{1/2})}\right)-\frac{\pi^{2}E_{1}}{2\beta_{1}^{4}}\left(\frac{1}{Y_{1}^{1/2}[(Y_{1}^{1/2}+X_{1}^{1/2})^{2}-E_{1}^{2}]}+\frac{1}{b[(b+X_{1}^{1/2})^{2}-E_{1}^{2}]}\right)$$

$$+\frac{\pi^{2}}{2(2-\delta_{1}^{2})\beta_{1}^{4}}\left(\frac{1}{X_{1}-(b-E_{1})^{2}}-\frac{1}{X_{1}-(Y_{1}^{1/2}-E_{1})^{2}}\right)+\frac{\pi^{2}(b-E_{1})}{2(2-\delta_{1}^{2})b\beta_{1}^{2}[X_{1}-(b-E_{1})^{2}]^{2}}$$

$$-\frac{\pi^{2}(E_{1}+X_{1}^{1/2})}{2(2-\delta_{1}^{2})X_{1}^{1/2}[b^{2}-(E_{1}+X_{1}^{1/2})^{2}]^{2}[Y_{1}-(E_{1}+X_{1}^{1/2})^{2}]}\right\} \quad , \quad (31)$$

where

 $D_1^2 = \frac{\beta_1^2 + b^2 \delta_1^2}{2 - \delta_1^2} > 0, E_1 = \frac{b(\delta_1^2 - 1)}{2 - \delta_1^2} > 0, \qquad X_1 = D_1^2 + E_1^2, \quad Y_1 = b^2 + \beta_1^2.$

The expressions for ΔE_2 and ΔE_4 , which are obtained from Eqs. (30) and (31), respectively, by interchanging the roles of m_1 and m_2 , are displayed explicitly in the Appendix. The ground-state energy of the exciton is now obtained by subtracting from the total energy of our system the minimum energies of the electron and the hole when these are free. The latter are just the self-energies of the electron polaron and the hole polaron. Thus the ground-state energy (E_B) of the exciton is given as

$$E_B = -(e^4 \mu/2\epsilon_{\infty}^2 \hbar^2) + \Delta E + \alpha_1 \hbar \omega + \alpha_2 \hbar \omega . \qquad (32)$$

DISCUSSION

We now use Eq. (32) to calculate the value of the ground-state energy of an exciton in various polar crystals and then compare it with its experimental values. Such a comparison along with the values of ΔE_1 , ΔE_2 , ΔE_3 , ΔE_4 , and ΔE is presented in Table II. The values of the various physical parameters used are given in Table I. In these materials the values of the electron band mass (m_1) and the coupling constant (α_1) are derived from the experimentally determined electron polaron masses. These masses are measured by cyclotron-resonance experiments and are therefore quite reliable. Similar measurements to determine the hole polaron masses have not been made, and therefore the values of m_2 and α_2 are known only approximately in these materials. As a matter of fact, in many polar crystals the hole polaron masses are derived from the experimentally determined values of the binding energy of an exciton using a hydrogenic formula with a reduced polaron mass and a static dielectric constant. This is probably a good procedure for weakly ionic crystals such as III-V compounds. However, as demonstrated by Bachrach and Brown, ¹⁰ this is not reliable for more polar materials. It is, therefore, difficult to estimate the accuracy of the hole masses derived in this manner. In view of this fact, we have used a somewhat different procedure to compare our theoretical results with experimental data. We assume that the experimental value of the ground-state energy of an exciton is given by

Eq. (32) and then derive the value of the hole coupling constant, referred to as $\alpha_2^{\text{theoret}}$ in Table II. We compare these values of α_2 with those that are estimated from experimental measurements in these polar crystals and find that these are in good agreement.

Equation (32) is based on the use of second-order perturbation theory and is, therefore, assumed to be valid for small values (≤ 1) of α_1 and α_2 . However, in the case of TlCl and TlBr, where the coupling constants are somewhat large, we also find a reasonably good agreement between our theory and experimental data. This may not be entirely unexpected. It is well known that second-order perturbation theory as applied to the free-polaron problem gives results which are valid for a much larger range of values of the coupling constant than one generally expects.¹⁸ For instance, one knows that the free-polaron mass as given by secondorder perturbation theory¹⁸ agrees very well with that derived from the path-integral method of Feynman¹⁹ for values of the coupling constants up to about 3 or so. Feynman's method is quite general and is valid for all values of the coupling constant. This suggests that even though we have a more

TABLE I. Values of static dielectric constant (ϵ_0) , optical dielectric constant (ϵ_{∞}) , electron-phonon coupling constant (α_1) , longitudinal-optical-phonon energy (\hbar_{ω}) , and experimental exciton binding energy (E_{E}^{expt}) .

Material	€₀	€∞	α1	$\hbar\omega$ (meV)	E_B^{expt} (meV)
TICI	37.6	5.1	2.40^{a}	21.5	11 ± 2^{a}
TlBr	35.1	5.4	2.10^{a}	14.3	6 ± 1^a
CdS	8.9	5.2	0.60 ^b	37.8	29.4 ^b
CdTe	10.9	7.2	0.35 ^b	21.3	10.0 ^b
AgBr	10.6	4.6	1.60°	17.4	16.4 ± 0.5^{d}

^aReference 10.

^bB. Segall and D. T. F. Marple, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. Prenner (North-Holland, Amsterdam, 1967), Chaps. 1 and 7.

^cJ. W. Bodby, Solid State Commun. <u>7</u>, 811 (1969). ^dReference 8.

TABLE II. Values of hole-phonon coupling constant $(\alpha_2^{\text{theoret}})$ calculated such that the theoretically calculated value of the ground-state energy (E_B) is equal to the experimental value (E_B^{expt}) , experimentally suggested values of hole-phonon coupling constant (α_2^{expt}) , and values of ΔE_1 , ΔE_2 , ΔE_3 , ΔE_4 , ΔE , and $-e^4\mu/2\epsilon_{\infty}^2\hbar^2$. All the energies are measured in units of meV.

Material	$lpha_2^{ theoret}$	α_2^{expt}	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE	$-rac{e^4\mu}{2\epsilon_\infty^2\hbar^2}$
TICI	4.90	4.2 ^a	-49.54	-206.50	69.90	152.90	-33.24	-133.69
TlBr	4.17	3.2 ^a	-31.03	-122.36	43.26	84.85	-25.28	-70.26
CdS	0.98	1.2 ^b	- 29.63	-78.25	34.87	41.22	-31.78	-57.11
CdTe	0.55	0.7 ± 0.2^{b}	-10.10	-20.62	9.05	8.99	-12.69	-15.23
AgBr	2.15	2.5 ± 0.3^{c}	- 31.63	-57.12	40.59	56.09	7.94	- 89.47

^aReference 10.

^bB. Segall and D. T. F. Marple, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. Prenner (North-Holland, Amsterdam, 1967), Chaps. 1 and 7.

^cReference 8.

complicated situation than that of a free polaron, our perturbation results as given by Eq. (32) may be valid for larger values of the coupling constants than are customarily regarded appropriate for perturbation theory.

In deriving Eq. (32) we have made use of two approximations. First, we have neglected the contribution of H_4 to E_B and second, we have replaced $[F, H_0]$ by $[F, p^2/2\mu]$. We know that in the limit of α_1 and α_2 going to zero, E_B is determined only by the relative coordinates. It is, therefore, reasonable to expect that neglecting H_4 will not make significant difference in E_B for small values of the coupling constants. Also, as we have stated earlier, E_B is the energy difference between the states of the exciton corresponding to n = 1 and $n = \infty$, and it is quite possible that H_4 will not contribute significantly to this quantity even when α_1 and α_2 are not too small. The second approximation that we have made is essentially the same as has been used in the calculation of the ground-state energy of the hydrogen atom in the presence of a uniform electric field using second-order perturbation theory in spherical coordinates.²⁰ One obtains a result which is identical to that obtained by the exact summation of the second-order perturbation term expressed in parabolic coordinates.²¹ Thus in this particular case, replacing $[F, H_0]$ by $[F, p^2/2\mu]$ is not an approximation. Recently, the energy spectrum of a polaron bound to a point defect via the Coulomb potential has been calculated using second-order perturbation theory, as formulated by Dalgarno and Lewis, ¹⁷ making the foregoing approximation.²² The theoretical results thus obtained agreed very well with the available experimental data. The exact second-order perturbation correction to the ground-state energy of a bound polaron has recently been evaluated numerically by Engineer and Tzoar.²³ They find that the results of Ref. 22 are in very good agreement with their exact results as long as the binding energy

of the polaron is comparable to or less than the longitudinal-optical-phonon energy. This suggests that the results of the present calculation should be quite good when the exciton binding energy is comparable to or less than $\hbar\omega$. In many materials of interest the binding energy of a Wannier exciton is less than $\hbar\omega$. Clearly, it is not possible to estimate the extent of inaccuracy introduced by these two approximations. The fact that there is a good agreement between our theoretical results and the experimental data suggests that the two approximations are rather reasonable. Efforts to get rid of the first approximation are currently in progress.

As we mentioned earlier, Bachrach and Brown¹⁰ have calculated variationally the values of the binding energy of an exciton in TlCl and TlBr using the following potential due to Haken²:

$$V(r) = -\frac{e^2}{\epsilon_{\infty}r} + \frac{e^2}{r} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0}\right) \left(1 - \frac{e^{-r/\beta_1} + e^{-r/\beta_2}}{2}\right).$$
(33)

Using a hydrogenic trial wave function with a single variational parameter and experimentally determined values of m_1 and m_2 , they calculate 94 and 48 meV as values of E_B in TlCl and TlBr, respectively. These are different from the experimental values by orders of magnitude. Haken's potential, which has been derived using the variational wave functions of Lee, Low, and Pines¹⁵ for small values of electron and hole wave vectors, is supposed to be quite good for shallow excitons, i.e., for excitons with a large electron-hole separation. In both TICI and TIBr the excitons are indeed shallow. It is therefore not clear to us why there is such an enormous difference between the theoretical and the experimental values in these materials. The effective interaction between the electron and the hole in a polar crystal as derived by Mahanti and Varma⁵ for the case when $E_B/\hbar\omega \ll 1$ seems to have an error, as pointed out recently by Sak.²⁴ They obtain a term of the form $1/r^2$, instead of a term

containing a contact interaction, in their effective interaction Hamiltonian. This, according to Sak, is due to an error in their evaluation of the contributions of two Feynman diagrams.

Finally, we would like to point out that the binding energy E_B as given by Eq. (32) is rather sensitive to small changes in m_1 and m_2 . Why this is so is not quite clear to us at this moment.

CONCLUSIONS

We have derived an analytic expression for the ground-state energy of a Wannier exciton interacting with the longitudinal-optical-phonon field of the crystal lattice. We have assumed that the coupling between the components of the exciton, i. e., the hole and the electron, and the optical-phonon field is weak and have, therefore, used second-order perturbation theory as formulated by Dalgarno and Lewis. We have briefly discussed the nature of the two approximations made during the course of our calculations. And finally, we have compared our theoretical results with the experimental data in various ionic crystals and found a good agreement. This suggests that the two approximations we have made are rather reasonable.

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APPENDIX: EVALUATION OF ΔE_1 , ΔE_2 , ΔE_3 , AND ΔE_4

Case 1: Evaluation of ΔE_1 and ΔE_2

To calculate ΔE_1 , for instance, we define a new vector $\vec{q}_1 = (m_2 / M)\vec{q}$ and express Eq. (26) in terms of this vector, i.e.,

$$\Delta E_1 = -\frac{2\mu U^2 M}{V\hbar^2 m_2} \sum_{\vec{\mathfrak{q}}_1} \sum_{\vec{\mathfrak{k}}} \frac{\langle i \, | \, \vec{\mathfrak{k}} \, \rangle \langle \, \vec{\mathfrak{k}} \, | \, i \, \rangle}{q_1^2 (q_1^2 - 2 \, \vec{\mathfrak{q}}_1 \cdot \vec{\mathfrak{k}} + 2\mu\omega/\hbar)} \,\,. \tag{A1}$$

Proceeding in a similar fashion, Eq. (27) may also be written as

$$\Delta E_2 = -\frac{2\mu U^2 M}{V\hbar^2 m_1} \sum_{\vec{q}_2} \sum_{\vec{k}} \frac{\langle i | \vec{k} \rangle \langle \vec{k} | i \rangle}{q_2^2 (q_2^2 - 2\vec{q}_2 \cdot \vec{k} + 2\mu\omega/\hbar)} ,$$
(A2)

where

$$\vec{\mathbf{q}}_2 = (m_1/M)\vec{\mathbf{q}}$$

In Eq. (A1) we convert the summation over \vec{q}_1 to an integral and take the principal value around the singularity. We get

$$\Delta E_{1} = -\frac{2\mu U^{2}M}{(2\pi)^{2}\hbar^{2}m_{2}} \left(\sum_{\vec{k}=0}^{|\vec{k}|=1/\beta} |\langle i | \vec{k} \rangle|^{2} \frac{\pi}{k} \sin^{-1}(k\beta) \right. \\ \left. + \sum_{|\vec{k}|=1/\beta}^{\infty} |\langle i | \vec{k} \rangle|^{2} \frac{\pi^{2}}{2k} \right) , \quad (A3)$$

where

 $\beta^2 = \hbar/2\mu\omega \; .$

Substituting the following expression for the Fourier transform of the ground-state wave function of the hydrogenic system, i.e.,

$$\langle i | \vec{\mathbf{k}} \rangle = 8 (\pi a^3 / V)^{1/2} (1 + a^2 k^2)^{-2},$$
 (A4)

into Eq. (A3), converting the summation over \vec{k} to an integral, replacing $\beta \vec{k}$ by \vec{K} , and integrating the second term in Eq. (A3) by parts, we obtain

$$\Delta E_{1} = -\frac{16\alpha_{1}\hbar\omega a}{3\pi\beta} \left(\frac{M}{m_{2}}\right)^{1/2} \times \int_{0}^{1} (1+K^{2})^{-1/2} \left(1+\frac{a^{2}K^{2}}{\beta^{2}}\right)^{-3} dK \quad (A5)$$

Here we have substituted for U from Eq. (2). The above expression for ΔE_1 is easily evaluated and yields Eq. (30).

From Eqs. (26) and (27) we notice that ΔE_2 can be obtained from ΔE_1 by interchanging the roles of m_1 and m_2 . Thus

$$\Delta E_2 = -\frac{8}{3} \alpha_2 \hbar \omega \frac{a}{\beta} \left(\frac{M}{m_1}\right)^{1/2} P_2 \left(\frac{1+a^2/2\beta^2}{(1+a^2/\beta^2)^{1/2}}\right).$$
(A6)

Case 2: Evaluation of ΔE_3 and ΔE_4

To calculate ΔE_3 , we substitute for $\langle \vec{k} | i \rangle$ and $\langle \vec{k} + \vec{q} | i \rangle$ from Eq. (A4) in Eq. (28) and obtain

$$\Delta E_{3} = -\frac{\gamma_{1}}{V^{2}} \sum_{\vec{k}} \sum_{\vec{k}} \frac{1}{q^{2} (b^{2} + k^{2})^{2} [b^{2} + (\vec{k} + \vec{q})^{2}]^{2}} \times \frac{1}{\delta_{1}^{2} q^{2} + 2\vec{k} \cdot \vec{q} - \beta_{1}^{2}} , \quad (A7)$$

where

$$\gamma_1 = 128 U^2 m_1 \pi / \hbar^2 a^5$$
, $\beta_1^2 = 2m_1 \omega / \hbar$,
 $\delta_1^2 = (2m_1 + m_2) / M$.



FIG. 1. Definition of the angles θ and ψ .

Transforming the summations over \bar{q} and \bar{k} into integrations in the usual manner and going over to the spherical coordinates for the \bar{k} variable, we may write ΔE_3 as follows:

$$\Delta E_{3} = -\frac{\gamma_{1}}{(2\pi)^{6}} \int \frac{d\tilde{q}}{q^{2}} \int_{0}^{\infty} \frac{k^{2}dk}{(b^{2}+k^{2})^{2}} \times \int_{0}^{\pi} \int_{0}^{2\pi} \frac{1}{(b^{2}+k^{2}+2qk\cos\theta+q^{2})^{2}}$$

$$\times \frac{1}{\delta_1^2 q^2 + 2qk\cos\theta - \beta_1^2}\sin\theta \,d\theta \,d\psi , \quad (A8)$$

where the angles θ and ψ are defined in Fig. 1. The integration over the angle variables is tedious but presents no special problems. We obtain, after carrying out this integration,

$$\Delta E_3 = \Delta M_1 + \Delta M_2 + \Delta M_3 , \qquad (A9)$$

$$\Delta M_1 = - \frac{\gamma_1}{(2\pi)^4} \int_0^\infty \frac{k \, dk}{(b^2 + k^2)^2} \int_{-\infty}^\infty \frac{1}{q \left[(\delta_1^2 - 1) q^2 - k^2 - (\beta_1^2 + b^2) \right]} \frac{1}{q^2 + k^2 - 2qk + b^2} \, dq , \qquad (A10)$$

$$\Delta M_2 = \frac{\gamma_1}{(2\pi)^4} \int_0^\infty \frac{k \, dk}{(k^2 + b^2)^2} \int_{-\infty}^\infty \frac{1}{q \left[(\delta_1^2 - 1) \, q^2 - k^2 - (\beta_1^2 + b^2) \right]^2} \, \ln(b^2 + k^2 + q^2 + 2 \, qk) \, dq , \qquad (A11)$$

$$\Delta M_{3} = -\frac{\gamma_{1}}{(2\pi)^{4}} \int_{0}^{\infty} \frac{k \, dk}{(k^{2} + b^{2})^{2}} \int_{-\infty}^{\infty} \frac{1}{q \left[(\delta_{1}^{2} - 1) \, q^{2} - k^{2} - (\beta_{1}^{2} + b^{2}) \right]^{2}} \ln(\delta_{1}^{2} q^{2} - \beta_{1}^{2} + 2qk) \, dq , \qquad (A12)$$

where we have interchanged the order of integration over q and k variables. The contributions of ΔM_1 , ΔM_2 , and ΔM_3 to ΔE_3 are evaluated analytically using the theory of complex variables. Such an evaluation, which is rather cumbersome, leads to Eq. (31).

If we compare the expressions of ΔE_3 and ΔE_4

as given by Eq. (23) and Eq. (24), respectively, we find that ΔE_4 can be obtained from ΔE_3 by interchanging the roles of m_1 and m_2 . Thus the final expression for ΔE_4 is the same as that for ΔE_3 except for the fact that m_1 and m_2 are interchanged. For the sake of completeness we write down explicitly for ΔE_4

$$\begin{split} \Delta E_4 &= \frac{-\gamma_2 \pi^2}{2(2\pi)^4 b(\delta_2^2 - 2)} \left(\frac{1}{8b^3 (D_2^2 + 2bE_2 - b^2)} - \frac{b - E_2}{2b^2 (D_2^2 + 2bE_2 - b^2)^2} + \frac{E_2 + X_2^{1/2}}{X_2^{1/2} (E_2 + X_2^{1/2} + b) \left[(E_2 + X_2^{1/2})^2 - b^2 \right]^2} \right) \\ &+ \frac{\gamma_2 \pi^2}{(2\pi)^4} \left[-\frac{2}{\beta_2^6} \ln \left(\frac{Y_2^{1/2}}{b} \right) + \frac{1}{b^2 \beta_2^4} - \frac{1}{2b^2 \beta_2^2 Y_2} \right] + \frac{\gamma_2}{(2\pi)^4} \left\{ -\frac{2\pi^2}{\beta_2^6} \ln \left[\frac{b + Y_2^{1/2}}{2b} \left(\frac{(Y_2^{1/2} + E_2 + X_2^{1/2}) (b - E_2 + X_2^{1/2})}{(b + E_2 + X_2^{1/2}) (Y_2^{1/2} - E_2 + X_2^{1/2})} \right)^{1/2} \right] \\ &+ \frac{\pi^2}{2\beta_2^4} \left(\frac{1}{2b^2} + \frac{1}{Y_2^{1/2} (b + Y_2^{1/2})} \right) - \frac{\pi^2 E_2}{2\beta_2^4} \left(\frac{1}{Y_2^{1/2} [(Y_2^{1/2} + X_2^{1/2})^2 - E_2^2]} + \frac{1}{b[(b + X_2^{1/2})^2 - E_2^2]} \right) \\ &+ \frac{\pi^2}{2(2 - \delta_2^2)\beta_2^4} \left(\frac{1}{X_2 - (b - E_2)^2} - \frac{1}{X_2 - (Y_2^{1/2} - E_2)^2} \right) + \frac{\pi^2 (b - E_2)}{2(2 - \delta_2^2) k_2^{1/2} [b^2 - (E_2 + X_2^{1/2})^2]^2 [Y_2 - (E_2 + X_2^{1/2})^2]} \right\} \quad , \quad (A13) \end{split}$$

where

 $\gamma_2 = \frac{128 U^2 m_2 \pi}{\hbar^2 a^5} , \quad \beta_2^2 = \frac{2m_2 \omega}{\hbar} , \quad \delta_2^2 = \frac{2m_2 + m_1}{m_1 + m_2} , \quad D_2^2 = \frac{\beta_2^2 + b^2 \delta_2^2}{2 - \delta_2^2} > 0, \quad E_2 = \frac{b(\delta_2^2 - 1)}{2 - \delta_2^2} > 0, \quad X_2 = D_2^2 + E_2^2 , \quad Y_2 = b^2 + \beta_2^2 .$

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PHYSICAL REVIEW B

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Quantum Dielectric Theory of Electronegativity in Covalent Systems. III. Pressure-Temperature Phase Diagrams, Heats of Mixing, and Distribution Coefficients

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Electronegativity difference was redefined in Paper I of this series as a scaling parameter which combines the concepts of valence and size differences. A procedure has been developed for its evaluation in terms of a two-band model. In Paper II of this series it was shown that this model describes and predicts the ionization potentials and electronic interband gaps of binary $A^N B^{8-N}$ compounds and their alloys. Here the energy of this model semiconducting-insulating solid is evaluated relative to a free-electron gas, i.e., an idealized metal, as a function of composition, pressure, and temperature. Using this highly simplified scaling approach, we obtain suprisingly accurate predictions for the heat of fusion, melting point, and pressure-temperature phase diagrams of these materials. A revised method of calculating the excess heat of mixing of a substitutional alloy is presented. This calculation is extended to the case of an arbitrary dilute impurity in an arbitrary semiconducting host; the distribution coefficient at the melting point of the host is obtained.

I. INTRODUCTION

In the first two papers of this series,^{1,2} hereafter referred to as I and II, the concept of electronegativity difference was defined as a scaling parameter which generalizes the concepts of valence and size differences in the manner proposed by Phillips.³ The theory was formulated in terms of the low-frequency electronic dielectric constant of a semiconductor $\epsilon(0) = n^2$, where *n* is the index of refraction below the band gap.

The treatment was restricted to diatomic crystals of formula $A^N B^{8-N}$ which form in the diamond, zinc-blende, wurtzite, and rocksalt structures. Thus only the sp^3 hybridized, or tetrahedral covalent bond, and, by extension, the predominately ionic p^3 octahedral bonding in the rocksalt structure was described. However, other authors4-8have discussed the extension of this formulation to several other classes of semiconductors-primarily in connection with nonlinear optical susceptibilities.⁹ Amorphous tetrahedral semiconductors have also been discussed.¹⁰⁻¹²

Unlike the electronegativity scales developed by Pauling¹³ and by Mulliken,¹⁴ the Phillips formulation³ defines the electronegativity difference C between ions to be dependent upon their crystalline environment¹ rather than simply the difference of elemental electronegativities. (C is in fact the dielectrically screened potential difference¹ between the fields produced by the ion cores of the two atoms participating in a given bond measured at the point of contact of their covalent radii.¹⁵ We refer to that point as the "bond site.")