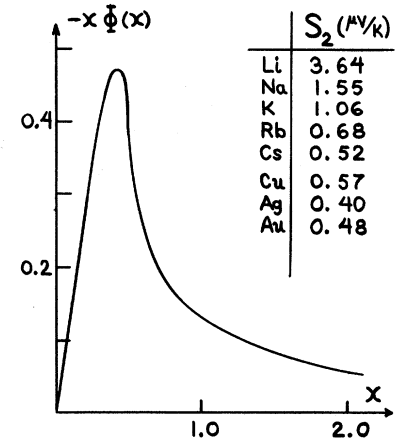

FIG. 3. Estimated PPD contribution to electron-diffusion thermopower.

with m/M the ratio of electronic to ionic masses, and N/N' the ratio of numbers of atoms to electrons. The function $\Phi(T/\Theta)$ is a complicated function of temperature that arises from the temperature dependences of the derivative of the Fermi function and of the amplitudes for phonon absorption and emission. It is easily shown that

$$\lim_{x\to 0} x\Phi(x) = \varphi_1 + \varphi_2 x^2$$

and

$$\lim_{x\to\infty} x\Phi(x) = \varphi_3 x^{-1},$$

with φ_1, φ_2, and φ_3 constants, so that the second term in (4) varies as T^3 and T^{-1} in the low- and high-temperature limits, just as phonon drag is normally predicted to vary.[1] Thus, while the first term in (4) exhibits the well-known linear temperature dependence, the second leads to a PPD effect. In Fig. 3 we show $-x\Phi(x)$ for a monovalent metal, and give some typical amplitudes S_2. It is clear from Fig. 3 that the PPD contribution to S is predicted to be of a shape and magnitude comparable with the experimentally observed "humps" that have previously been attributed solely to phonon drag. Thus, an inclusion of these effects is essential if valid conclusions are to be drawn from existing experimental data.

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†National Science Foundation Predoctoral Fellow.

‡Present address: Air Force Weapons Laboratory, Kirtland Air Force Base, N. Mex. 87117.

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DIRECT EXCITON SPECTRUM IN DIAMOND AND ZINC-BLENDE SEMICONDUCTORS*

A. Baldereschi and Nunzio O. Lipari
Physics Department and Material Research Laboratory, University of Illinois, Urbana, Illinois 61801

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We present a new method to investigate the exciton spectrum in the case of degenerate bands. Using symmetry considerations and second-order perturbation theory, we obtain a simple analytical expression for the binding energy as a function of the band parameters. Direct excitons in group IV elements, III-V compounds, and II-VI compounds can be investigated by this method. Results are given for Ge, GaAs, InSb, ZnSe, and CdTe.

Effects due to direct exciton formation have been observed in many crystals with the diamond and the zinc-blende structure. Since the first observation by Macfarlane et al.[1] and Zwerdling, Roth, and Lax[2] of the direct exciton in Ge, many authors have investigated direct excitons in III-V[3] and II-VI[4] compounds. In substances where the exciton has a small binding energy and cannot be observed directly, effects due to exciton formation have been observed in magneto-optical experiments[5] and an estimate of the binding energy is possible.

In contrast to such abundance of experimental data, little theoretical work has been done up to date and, in most cases, only rough estimates of the binding energy are available.[6] Exciton theory has been developed in detail[7] for crystals with simple valence and conduction bands. In this case the exciton Hamiltonian can be reduced to that of the hydrogen atom and exact solutions are obtained. However, crystals with the diamond and zinc-blende structure have a degenerate valence band at $\vec{k}=0$, where the exciton is formed, and therefore the theory for simple bands cannot be applied.

The exciton Hamiltonian in the case of degenerate bands has been derived by Dresselhaus[8] but, because of its complexity, no exact solutions are known. McLean and Loudon[9] have obtained an approximate solution for the ground state of the exciton in Ge using a variational technique previously introduced by Kohn and Schechter.[10] The same method was also used by Abe[11] who considered the direct exciton in Ge and GaAs. This method involves elaborate computations for the ground state and becomes practically impossible for excited states. For this reason the method has not been applied to other crystals where instead estimates of the binding energy have been obtained using a simple model in which the degenerate valence band is replaced by an "average" simple band.

Valence-band parameters are now available for crystals with the diamond and zinc-blende structures and therefore it would be desirable to obtain values of the exciton binding energy which take into account the details of the valence band. In this Letter we give a simple analytical expression for the binding energy of the direct exciton which is valid for all crystals with the diamond and zinc-blende structures. This expression takes into full account all the details of the degenerate valence band and its results are as accurate as those obtained using the variational method.

Crystals with diamond and zinc-blende lattices have very similar band structures.[12] The direct gap is at $\vec{k}=0$ where the conduction band has a nondegenerate minimum and the valence band has a threefold degenerate maximum (neglecting spin). When spin is included, the valence band becomes sixfold degenerate and is split by spin-orbit interaction into an upper fourfold and a lower twofold degenerate band separated by a spin-orbit splitting Δ.

For this kind of band structure, the Hamiltonian for the relative electron-hole motion is (neglecting the electronic spin)[8]

$$H_{\mathrm{ex}}=[p^2/2m_e^*-e^2/\epsilon r]I-H_v(\vec{p}),\tag{1}$$

where $\vec{p}$ is the relative electron-hole momentum, m_e^* is the electron effective mass, ϵ is the static dielectric constant, r is the electron-hole distance, I is the 6×6 unit matrix, and H_v is the well known 6×6 matrix which describes the hole kinetic energy near $\vec{k}=0$ and is given, e.g., by Kane.[13]

In all crystals that we are considering, the spin-orbit splitting Δ is much larger than the exciton binding energy and we can neglect the effects of the split-off valence band and reduce the Hamiltonian (1) to the following 4×4 matrix:

$$H_{\mathrm{ex}}=\begin{bmatrix} P+Q & L+U & M-U & \sqrt{3}U^+ \\ L^++U^+ & P-Q & -\sqrt{3}U & M+V \\ M^+-V^+ & -\sqrt{3}U^+ & P-Q & U-L \\ \sqrt{3}U & M^++V^+ & U^+-L^+ & P+Q \end{bmatrix}\tag{2}$$

where we have defined

$$P=\frac{p_x^2+p_y^2+p_z^2}{2\mu_0}-\frac{e^2}{\epsilon r}\quad (s\text{-like}),\tag{3a}$$

$$Q=\frac{p_x^2+p_y^2-2p_z^2}{2\mu_1}\quad (d\text{-like}),\tag{3b}$$

$$L=-i\frac{(p_x-ip_y)p_z}{2\mu_2}\quad (d\text{-like}),\tag{3c}$$

$$M=\sqrt{3}\frac{p_x^2-p_y^2}{2\mu_1}-i\frac{p_xp_y}{2\mu_2}\quad (d\text{-like}),\tag{3d}$$

$$U=i\frac{\sqrt{3}}{2}\frac{1}{a_0}\frac{p_x+ip_y}{2\mu_3}\quad (p\text{-like}),\tag{3e}$$

$$V=-\sqrt{3}\frac{1}{a_0}\frac{p_z}{2\mu_3}\quad (p\text{-like}),\tag{3f}$$

$a_0=\epsilon\hbar^2/(\mu_0e^2)$ being the Bohr radius relative to an effective mass μ_0 and to a dielectric constant ϵ. In the above formulas we have introduced the masses μ_0, μ_1, μ_2, and μ_3 which are the most natural choice for the description of the valence and conduction bands in the exciton Hamiltonian. They are related to the Buttinger parameters[14] γ_1, γ_2, and γ_3 as follows:

$$1/\mu_0=1/m_e^*+\gamma_1/m_0,\tag{4a}$$

$$1/\mu_1=\gamma_2/m_0,\tag{4b}$$

$$1/\mu_2=(6/\sqrt{3})\gamma_3/m_0,\tag{4c}$$

where m_0 is the free-electron mass. The effective mass μ_3, which describes the effects of inversion asymmetry, is infinite for diamond lattices and generally large for zinc-blende lattices.

We note that, under the operations of the rotation group, the operators (3a)-(3f) have different symmetry properties which are indicated on their right. In accordance with this, it is natural to write (2) as

$$H_{\mathrm{ex}}=H_s+H_p+H_d,\tag{5}$$

where H_s, H_p, H_d are 4×4 matrices which contain only s-like, p-like, and d-like operators, respectively. The three terms in Hamiltonian (5) have a simple physical meaning. The first term represents an exciton which results from the Coulomb interaction between the electron and the isotropic part of the hole. H_d describes the effect of the anisotropy in the valence band, and H_p the effects of inversion asymmetry.

To solve the Hamiltonian (5) we note that, from experimental data, both H_p and H_d produce small effects so that we can consider them as a perturbation with respect to H_s. Exact eigenfunctions and eigenvalues of the unperturbed Hamiltonian H_s are very easily found because the operator H_s can be written as the product of the 4×4 unit matrix times the Hamiltonian of a hydrogen atom with reduced mass μ_0 and dielectric constant ϵ. Including now H_p and H_d as a perturbation, it is easily seen that, for the ground state, the first nonvanishing contribution comes from second-order perturbation theory. After straightforward but lengthy calculations[15] we obtain for the binding energy

$$E_b = R_0\left[1+\frac{10}{7}\left(\frac{\mu_0}{\mu_1}\right)^2+\frac{5}{28}\left(\frac{\mu_0}{\mu_2}\right)^2+\frac{9}{4}\left(\frac{\mu_0}{\mu_3}\right)^2\right], \qquad (6)$$

where $R_0=\mu_0e^4/(2\hbar^2\epsilon^2)$ is the Rydberg relative to an effective mass μ_0 and to a dielectric constant ϵ. In expression (6) the first term comes from the isotropic part of the Hamiltonian, the second and the third terms represent the effect of the anisotropy, and the last term represents inversion asymmetry effects.

We have applied expression (6) to a few group-IV elements, III-V compounds, and II-VI compounds, and the results are shown in Table I together with the band parameters and the dielectric constants used in the calculation. The results shown in Table I have been obtained neglecting the contribution from the last term in expression (6) in view of the fact that the inversion asymmetry effective mass μ_3 is known neither experimentally or theoretically. The only crystal for which this parameter had been estimated is InSb where Pidgeon and Groves[20] give $\mu_3=0.872m_0$. Assuming this value, we find a correction of 0.0005 meV to the binding energy. Even considering a large uncertainty for the value of μ_3 given above, it is clear that the inversion-asymmetry contribution to the binding energy is very small, thus supporting our assumption of treating H_p in the Hamiltonian (5) as a perturbation. From Table I we also see that the anisotropy contribution E_d is small and therefore our perturbation treatment is completely valid. Furthermore, our results are as accurate as those obtained by the variational method as is shown by the first two columns of Table I. In fact for Ge and GaAs we have used the same parameters used by Abe[11] and our results are in complete agreement with those obtained with the variational approach. The agreement of our results with experimental estimates of the binding energy is satisfactory and could be improved by using more accurate valence band parameters.

It is to be mentioned that our method cannot be applied, as it is, to the problem of indirect excitons or to that of acceptor states because in these cases the anisotropy term in the Hamiltonian (5) can be so large that perturbation theory is not valid. However, our method can be extended to any number of degenerate bands and any kind of crystal symmetry as long as terms of lower symmetry in the Hamiltonian (5) can be treated by perturbation theory. For example, the method could be applied directly to the general Hamiltonian (1) to include the contribution of the split-off valence band. Finally, the method

Table I. Exciton binding energy E_b and anisotropic contribution E_d to the binding energy as calculated from expression (6) using the band parameters m_e^*, μ_0, μ_1, and μ_2 and the dielectric constant ϵ. The energy unit is meV and m_0 is the free electron mass.

	Ge	GaAs	InSb	ZnSe	CdTe
ϵ	16.0 (Ref. 11)	12.9 (Ref. 11)	16.8 (Ref. 17)	8.66 (Ref. 4)	9.65 (Ref. 4)
m_e^*/m_0	0.037 (Ref. 11)	0.072 (Ref. 11)	0.015 (Ref. 16)	0.170 (Ref. 16)	0.096 (Ref. 16)
μ_0/m_0	0.025 (Ref. 11)	0.049 (Ref. 11)	0.011 (Ref. 16)	0.125 (Ref. 16)	0.079 (Ref. 16)
μ_1/m_0	0.224 (Ref. 11)	0.652 (Ref. 11)	0.117 (Ref. 16)	4.167 (Ref. 16)	1.754 (Ref. 16)
μ_2/m_0	0.051 (Ref. 11)	0.095 (Ref. 11)	0.032 (Ref. 16)	0.425 (Ref. 16)	0.338 (Ref. 16)
E_d	0.08	0.22	0.02	0.38	0.15
E_b (theor)	1.40	4.22	0.57	23.06	11.69
E_b (exp)	1.2 (Ref. 18)	3.4 (Ref. 19)	···	19 (Ref. 4)	10 (Ref. 4)

can also be applied to excited states, which have been experimentally observed in some of the II-VI compounds.[4]

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ROLE OF PHONONS AND BAND STRUCTURE IN METAL-INSULATOR PHASE TRANSITION*†

D. C. Mattis
Belfer Graduate School of Science, Yeshiva University, New York, New York 10033

and

W. D. Langer
Goddard Institute for Space Studies, NASA, 2880 Broadway, New York, New York 10025

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We present a soluble model of electrons interacting with lattice vibrations which displays metallic, superconducting, and insulating phases. We solve the thermodynamics of this model and discuss its properties. The metal-insulator phase transition is second order for sc and bcc tight-binding bands. With sufficient deviation [(5-10)% for coupling constant $\bar{g}=0.1$] from such band structure the transition becomes first order. Above this, the "collective insulator" ceases to exist. Our model might apply to certain transition-series metal oxides, such as VO_2.

We treat several aspects of a soluble model which exhibits an insulator-metal phase transition, polaron effects, low mobility, and a tendency toward superconductivity. This model has several features of certain transition-series oxides such as Ti_2O_3 and VO_2.[1,2] Unlike the Hubbard model,[3,4] the present model has no significant magnetic properties, so that it is only applicable to nonmagnetic oxides.[4,5] Based as it is on the electron-phonon interaction, we believe this model to apply when the effective coupling parameter $\bar{g}=g^2/\hbar\omega$ exceeds the Coulomb parameter U by a sufficient amount so that qualitatively it is legitimate to ignore U. Otherwise, the Hubbard model is applicable and one obtains antiferromagnetic ordering in the ground state.[4,6] In the present model, the ground-state insulating phase is associated with finite crystallographic distortion, whereby the unit cell is doubled. The bands then split and what might have been mistaken for a metal with a half-filled band becomes an insulator. Moreover, the density of states near the band edges become anomalously large, resulting in surprising thermodynamic and transport properties. We shall later show that the details of the metal-insulator phase transition depend sensitively on band structure. At first, however, we assume a high-