*Laboratoire associé au Centre National de la Recherche Scientifique.
[1]E. Fawcett, Phys. Rev. B 2, 1604 (1970).
[2]E. Fawcett, Phys. Rev. B 2, 3887 (1970).
[3]R. Keller, J. Ortelli, and M. Peter, Phys. Letters 31A, 376 (1970).
[4]A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).
[5]P. Ségransan, J. C. Fanton, and P. Averbuch, Solid State Commun. 8, 1151 (1970).
[6]P. Ségransan and P. Averbuch, Proceedings of the Sixteenth Colloque AMPERE, Bucharest, 1970 (unpublished).
[7]T. H. Brown and P. J. Green, Phys. Letters 31A, 148 (1970).

PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Thickness Dependence of the Ground-State Exciton Energy in WSe_2 †

G. Jones
Département de Physique, Université de Montréal, Montréal, Québec, Canada
(Received 19 May 1971)

A theory developed for a thin anisotropic semiconductor, where the exciton is treated in the effective-mass approximation and where the effect of crystal surfaces is included by means of image-charge potentials, is applied to crystals of thickness less than 500 Å. The theory leads to an exciton ground-state energy which closely approaches an inverse-square-law dependence on thickness. By the use of estimates of the dielectric and reduced-exciton-mass components quantitative agreement with data on WSe_2 is obtained.

Recent developments in the theory of the effect of finite crystal size on the exciton-energy spectra have been made by Jones and Brebner[1] (hereafter called I) and Bendow.[2] Both these papers use image potentials to account for the effect of the surfaces on the exciton- and impurity-electron systems, respectively. In the present paper we utilize the theory of I in making a comparison with the recent experimental data of Consadori and Frindt[3] on the exciton-absorption spectrum in very thin crystals of WSe_2.

The Schrödinger equation for an exciton in a uniaxial crystal with the z direction along the c axis and normal to the plane-parallel interfaces a distance $2L$ apart is, in transformed coordinates,[4]

$$\frac{-\hbar^2}{2\mu_\perp}\nabla_{r'}^2\Psi-\frac{\hbar^2}{2M_\perp}\left(\frac{\partial^2}{\partial X'^2}+\frac{\partial^2}{\partial Y'^2}\right)\Psi-\frac{\hbar^2\beta^2}{2M_\parallel}\frac{\partial^2}{\partial Z'^2}\Psi-\left[\frac{e^2}{4\pi\epsilon_0[\epsilon_\perp\epsilon_\parallel(x'^2+y'^2+\gamma'^2z'^2)]^{1/2}}-U_L'-U_R'\right]\Psi=E\Psi\,, \tag{1}$$

where

$$\gamma=\left(\frac{\epsilon_\perp\mu_\perp}{\epsilon_\parallel\mu_\parallel}\right)^{1/2},\quad \beta=\left(\frac{\mu_\parallel}{\mu_\perp}\right)^{1/2}.$$

$\vec{r}'(x', y', z')$ and $\vec{R}'(X', Y', Z')$ are the relative and center-of-mass coordinates, respectively, of the exciton. U_L' and U_R' are the image-charge potentials; these and other quantities are defined in I.

We neglect the contribution from the center of mass in the X' and Y' directions and write

$$\Psi=\phi_n(x', y', z', Z')F(Z')\,. \tag{2}$$

On separation under the adiabatic approximation we obtain for the case $\gamma=1$

$$-\nabla_t^2\phi_n-(2/t-U_L''-U_R'')\phi_n=\xi_n(D')\phi_n\,, \tag{3}$$

$$-\frac{d^2F}{dD'^2}+\left(\frac{M_\parallel}{\mu_\parallel}\right)[\xi_n(D')-G]F=0\,, \tag{4}$$

where

$$t=r'/a_0\,,\quad D'=Z'/a_0\,,\quad a_0=4\pi\hbar^2\epsilon_0(\epsilon_\perp\epsilon_\parallel)^{1/2}/\mu_\perp e^2$$

is the effective exciton Bohr radius. The quantities denoting energy in Eqs. (3) and (4) are now expressed in exciton-rydberg units, having been multiplied by T where

$$T=8\pi\epsilon_0(\epsilon_\perp\epsilon_\parallel)^{1/2}a_0/e^2 \tag{5}$$

and, in particular,

$$U_i''=U_i'T\quad(i=L, R)\,.$$

Since we are interested here in the ground-state exciton, we need only consider the case $n=1$ and employ the trial wave function (see I)

$$\phi_1 = (D' + m_2' z')(D' - m_1' z')(H' - m_2' z')$$

$$\times (H' + m_1' z')\, e^{-\delta_1 r'}, \qquad (6)$$

where $H' = (2L' - Z')/a_0$ and δ_1 is the variation parameter with respect to which $\xi_1(D')$ is minimized.

The procedure of I is followed for the evaluation of $\xi_1(D')$, the potential which governs the center-of-mass motion of the exciton, and the eigenvalues G of Eq. (4) obtained. The results are presented in Fig. 1 for the case $m_1' = 0.25$, $m_2' = 0.75$, [5] and show the thickness dependence of G for the $n = 1$ exciton in the transformed coordinate system.

There are a number of approximations that have been made in developing the theory. One of these is the neglect of all image-charge pairs except the one closest to each crystal interface. By considering the problem in terms of dipole-dipole interactions the contribution of the neglected dipoles to the energy is found to be less than 13% of that due to the first dipole pair, for $L' = a_0$ and $W = 1$. We may assume that the quantum-mechanical calculation has a similar error due to the neglected image-charge pairs and that it would then be 13% of the difference in G for $W = 0$ and $W = 1$. Since realistic values of W are almost certainly < 0.8, the error arising from the neglected dipoles is $< 10\%$.

It has been shown in I that although the form of $\xi_n(D')$ depends strongly on the ratio m_1'/m_2', the eigenvalue G is much less sensitive. Calculations indicate that the eigenvalue results for G are within ~ 0.1 exciton rydbergs of those of Fig. 1 for the mass-ratio (m_1'/m_2') range 0.05–1.0.[6] The mass ratio of $\frac{1}{3}$ used in obtaining the results of Fig. 1

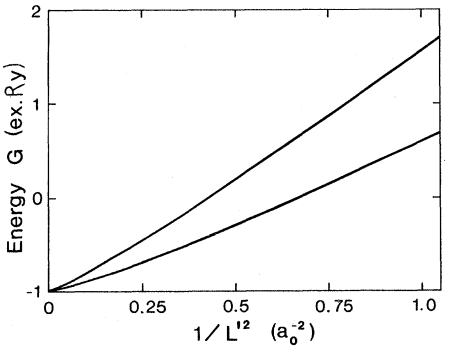

FIG. 1. Theoretical results in the transformed coordinate system showing the dependence of energy G, in exciton rydbergs, on the inverse square of the crystal half-width L', where L' is in units of a_0, the exciton Bohr radius. The upper curve is calculated using $W = 1$ and the lower using $W = 0$, and they represent the two extreme cases with or without image-charge contributions, respectively. Other parameters used are $n = 1$, $m_1' = 0.25$, and $m_2' = 0.75$.

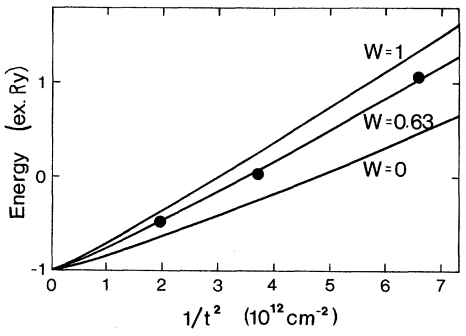

FIG. 2. Comparison of theory with experiment where the parameters used in the calculation are $n = 1$, $m_1' = 0.25$, $m_2' = 0.75$, $a_0 = 33.5$ Å, and $\beta^2 = 3.2$. The closed circles represent experimental data of Consadori and Frindt (Ref. 3) for the A-exciton ground state $(n = 1)$ in WSe_2. The curve calculated with $W = 0.63$ best fits these data.

was chosen because it lies near the middle of this range both in terms of mass and in the resulting eigenvalues G.

The validity of the adiabatic approximation, used in obtaining Eqs. (3) and (4), is subject to the condition that the correction energy $\Delta\xi_1(D')$, arising from the nonadiabatic terms, be much smaller than $\xi_1(D')$ where

$$\Delta\xi_1(D') = -\left(\frac{\mu_\parallel}{M_\parallel}\right)\left[\int \phi_1^* \frac{d^2}{dD'^2}\phi_1 dt^3 + \frac{2}{F}\frac{dF}{dD'}\int \phi_1^* \frac{d}{dD'}\phi_1\, dt^3\right]. \qquad (7)$$

This correction increases with decreasing L' and is almost directly proportional to the term $m_1' m_2'$. While for the case $L' = a_0$, $m_1'/m_2' = 1.0$ the values of $\Delta\xi_1(D')$ are not much smaller than $\xi_1(D')$; for $L' = a_0$, $m_1'/m_2' = 0.05$ the value obtained for G (for $W = 1$) of 1.55 exciton rydbergs is only reduced by 0.04 exciton rydbergs when the correction $\Delta\xi_1(D')$ is neglected. Thus, although at one end of the mass-ratio range the adiabatic correction is large, at the other end it is small and from what has been noted previously regarding the insensitivity of G to the mass ratio m_1'/m_2', the error due to the adiabatic approximation in the results of Fig. 1 is less than ~ 0.15 exciton rydbergs.

From the above we conclude that the inclusion of results for $L' = a_0$ in Fig. 1 is justified, but that they are too inaccurate below this value of L'.

In order to compare the theoretical results of Fig. 1 with the experimental data of Consadori and Frindt we have first to transform to real space

and also convert the units of a_0 into angstroms. For this we require the quantities $\mu_\perp$, $\mu_\parallel$, $\epsilon_\perp$, and $\epsilon_\parallel$, which as far as we are aware have not been measured in WSe_2. However, the bulk crystal binding energy of the A exciton in WSe_2 is known, and using a value of 0.05 eV (Consadori and Frindt[3]) in Eq. (5), we obtain

$$a_0 = 144/(\epsilon_\perp \epsilon_\parallel)^{1/2}\ \text{Å}\ . \tag{8}$$

The layer structure WSe_2 is one of the regular TX_2 transition-metal dichalcogenides and it is grouped in the review by Wilson and Yoffe[7] as belonging to the group-VI trigonal-prism compounds which include MoS_2. The spectra of WSe_2 and MoS_2 show a number of similarities and we have assumed that the dielectric components are also similar.[8] Using the values given by Evans and Young[9] of $\epsilon_\perp = 6.76$ and $\epsilon_\parallel = 2.74$, we obtain

$$a_0 = 33.5\ \text{Å}\ . \tag{9}$$

For these values of the dielectric components a value of W of approximately 0.6 would lie midway between the extreme limits for W (Appendix II in I). By using this value of W, and choosing $\beta^2 = 3.2$, we obtain the results shown in Fig. 2 in comparison with the data taken from Fig. 3 of Consadori and Frindt for WSe_2. The original data based on estimated thickness,[10] obtained before conversion to thicknesses which are integer multiples of a single WSe_2 layer of 6.5 Å, suggest that a value of $\beta^2 = 4.5$ may be more suitable.

In conclusion we point out that the theory leads to an energy which closely approaches an inverse-square-law dependence on thickness. By using estimates of the dielectric and reduced-exciton-mass components, we obtain quantitative agreement with data on WSe_2.

The author wishes to thank Dr. J. L. Brebner for his encouragement and many helpful suggestions.

---

†Work supported by the National Research Council of Canada.

[1]G. Jones and J. L. Brebner, J. Phys. C 4, 723 (1971).

[2]B. Bendow, Phys. Rev. B 3, 1999 (1971).

[3]F. Consadori and R. F. Frindt, Phys. Rev. B 2, 4893 (1970).

[4]See I. Essentially this means that results calculated in the transformed coordinate system apply to crystals of half-width $L = L'/\beta$, where L' is the half-width in the transformed coordinate system.

[5]The reason for these values is explained later in the text.

[6]Except for the L' range near a_0 where the adiabatic approximation makes this difficult to determine—see text.

[7]J. A. Wilson and A. D. Yoffe, Advan. Phys. 18, 193 (1969).

[8]Consadori and Frindt (Ref. 3) use the refractive index of MoS_2 in their crystal-thickness determination.

[9]B. L. Evans and P. A. Young, Phys. Status Solidi 25, 417 (1968).

[10]F. Consadori (private communication).

PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Role of Peripheral Phonons in the Lattice Thermal Conductivity of Doped Semiconductors: Application to *n*-Ge

K. S. Dubey and G. S. Verma
Physics Department, Banaras Hindu University, Varanasi-5, India
(Received 6 April 1971)

In the present paper we have studied the role of peripheral phonons in the phonon conductivity of doped semiconductors. For this purpose we have taken Callaway's model and we have also separated the contributions of the phonons which are interacting with electrons and of the peripheral phonons. The temperature which differentiates the peripheral phonons from other phonons is given by $\Theta^* = (2F\hbar v_s/k_B)(\pi^2 n)^{1/3}$, where the factor F varies from 3 to 5 for different Sb- and As-doped Ge samples. Excellent agreement between the theoretical and experimental values of phonon conductivity is obtained.

Recently Gaur and Verma[1] established that for those semiconductors for which the donor-electron concentration is greater than 10^{17} cm^{-3} and for which the donor levels merge with the conduction band, Ziman's scattering of phonons by conduction electrons is the relevant phonon scattering mechanism. This is the explanation of the drastic reduction in the phonon conductivity of Sb- and As-doped Ge as observed by Goff and Pearlman.[2] However, Gaur and Verma could not explain the results below 10 °K. They could improve the agreement between theory and experiment only by lowering τ_{ep}^{-1} by a factor of 10 or 30. Recently Singh and Verma[3] have shown that excellent agree-