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THE ELECTRONIC ABSORPTION EDGE IN STRONGLY ANISOTROPIC SUBSTANCES

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Several recent experiments have been reported concerning the optical absorption spectra of layered crystals, notably GaSe [1]. In these crystals, the structure consists of fourfold layers, the bonding between the layers being of the van der Waals type while the intra layer bonding is largely covalent. In the tight binding approximation, this implies that the electronic bands, in directions in k-space perpendicular to the layers will be very flat and consequently will have a large effective mass in that direction. The normal Elliott [2] theory of excitons is now no longer applicable because of the strong anisotropy, but one approximate way of taking this into account is to assume that the inverse effective mass tensor is diagonal with the zz component zero. The equation of the function which describes relative motion of the electron and hole is now

$$\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) F - e^2 F |\kappa^2 \sqrt{r^2 + z^2} = EF$$

where $r^2 = x^2 + y^2$ and $\kappa$ is the (assumed isotropic) dielectric constant of the crystal. Solutions of the equation are of the form $F(x, y) \delta(z - z_0)$ where $z_0$ is a good quantum number, and the function represents the electron and hole moving with a constant separation in the z-direction.

For direct optical transitions to occur the electron and hole must occupy the same site, so for these optical properties one may take $z_0 = 0$ and one obtains the two dimensional hydrogen equation. In radial coordinates this is separable :

$$F(r) = f(r) \frac{e^{imb}}{\sqrt{2\pi}}$$

where $f(r)$ satisfies

$$-\frac{\hbar^2}{2\mu} \left( \frac{1}{r} \frac{d}{dr} \left( r \frac{d}{dr} \right) - \frac{m^2}{r^2} \right) f - \frac{e^2 f}{k r} = Ef.$$  (3)

By making the substitution $\varphi = e^{-r^2/2} f$ where $\rho_2$ is the length measured in Bohr radii, $\rho = r/a\lambda$, $a = \kappa \hbar^2/\mu e^2$ and $\lambda = \sqrt{-R/4E}$ where $R$ is the Rydberg, $R = \mu e^4/2 \hbar^2 \kappa^2$ we obtain a form of Laguerre’s equation

$$\rho \frac{d^2 \varphi}{d\rho^2} + (1 - \rho) \frac{d\varphi}{d\rho} + \left( 2 \lambda - \frac{1}{2} \frac{m^2}{\rho} \right) \varphi = 0. \quad (4)$$

For bound excitons, $E < 0$, the energies are in the series $E_n = R/(n + \frac{1}{2})^2$ where $n = 0, 1, ..., etc$. The oscillator strengths which are proportional to $|f(0)|^2$ depend on $n$ like $1/(n + \frac{1}{2})$ while for energies above the gap the absorption coefficient is modified by a Sommerfeld factor $\exp(\pi \sqrt{R/\varepsilon})/\cosh(\pi \sqrt{R/\varepsilon})$ where $\varepsilon = h\nu - E_g$.

For large values of $n$ the bound exciton absorption merges continuously into that due to the continuum states above the band edge. This leads to a featureless spectrum near the edge; the small hump predicted by the theory of Shinada and Sugano [3] is brought about by the assumption of a non constant matrix element, which ought then to have been introduced earlier into the theory.

With the polarisation vector of the light in the x, y plane and a forbidden direct transition for this polarisation, the intensity of absorption is proportional to the gradient of $f$ in the direction of polarisation. In this case the $n = 0$ exciton has zero gradient and the energies of the weakly allowed transitions are

$$E_n = R/(n + \frac{1}{2})^2, \quad n = 1, 2, ..., $$

and their oscillator strengths depend on $n$ like

$$n(n - 1)(n - \frac{1}{2})^5.$$  

In this case the Sommerfeld factor is

$$(R + \varepsilon/4) \exp \pi \sqrt{R/\varepsilon} \cosh \pi \sqrt{R/\varepsilon}$$

and joins continuously on to the quasi-continuum of high $n$ exciton states.

It should be pointed out that besides being perturbed by the usual change in the effective dielectric constant,
the \( n = 0 \) exciton will have a much more three-dimensional character as it could be confined to within the thickness of the crystal layers. This in itself would raise the energy of the \( n = 0 \) exciton from \(-4R\) toward \(-R\).

The effective dielectric constant will, of course, also be highly anisotropic. The solution of Maxwell’s equation

\[
\nabla \cdot D = \nabla \cdot (\kappa \nabla \phi) = 4\pi \delta(r) \tag{5}
\]

is

\[
\phi = \frac{1}{\sqrt{\kappa_x \kappa_z \sqrt{r^2 + z^2} \kappa_x^{-2} \kappa_z^{-2}}}
\]

so the effective dielectric constant to use is \( \sqrt{\kappa_x \kappa_z} \). This effect to some extent explains the lack of success of this model as the anisotropy of the dielectric constant tends to counteract that of the effective mass. Indeed, for the special case \( \mu_x/\mu_z = \kappa_x/\kappa_z \) the Schrödinger equation may be solved exactly. In this case the excitons are very much flattened in the \( z \)-direction, but appear at the energies corresponding to the normal three-dimensional case, \( E_g = R/n^2 \) where \( R = \mu_x e^4/2 \hbar \kappa_x \kappa_{xz} \), and this could explain the good agreement found with the conventional formula for MoS\(_2\).

Bibliographie


DISCUSSION

F. BASSANI. — Have you compared your theory with the experimental data available in GaSe for the exciton lines and the modification of the continuum absorption due to the hole-electron interaction?

C. SENNETT. — We have attempted only a fitting of the energy levels in GaSe to the \( 1/(n + 1/2)^2 \) formula, without considering the effect on the continuum absorption. In this case the agreement is not good, but it is not expected to be because of the small number of lines observed, and the fitting to either the isotropic or the strongly anisotropic formulae is about equally bad.

S. NIKITINE. — La théorie que vous exposez est très intéressante. Quelle est la valeur absolue des intensités d’oscillateur des deux classes de transitions. Sont-elles comparables aux valeurs trouvées dans la théorie d’Elliott?

C. SENNETT. — Elles sont du même ordre de grandeur.