Translational Mass of an Exciton

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From transmission electron-energy-loss measurements we show that the mass of an exciton M^* is greater than the sum of the effective masses of the electron and hole $m_e + m_h$. This result is consistent with a recent prediction by Mattis and Gallinar.

Valence excitons in semiconductors and insulators have been studied theoretically and experimentally for many years. The two most widely used theoretical models are due to Frenkel, appropriate for tightly bound, small excitons, and to Wannier and Mott, appropriate for more loosely bound excitons with wave functions extending over many unit cells in the crystal. In spite of the fact that much work has been done by use of both of these models over many years, a new and surprising result was obtained recently by Mattis and Gallinar.[1] They addressed the question of the translational mass of the exciton. According to the standard treatment in the effective-mass approximation this is simply the sum of the electron and hole masses. That is, the translational mass of the exciton and the mass of an unbound electron-hole pair are the same. That result is straightforward and seemingly inflexible. It is consistent with all that we know about nonrelativistic dynamics. According to Galilean invariance, internal forces in a composite system do not affect the motion of the center of mass and the total mass is the sum of the masses of the particles in the system.

Mattis and Gallinar show that the translational mass of an exciton is greater than the sum of the electron and hole masses. Their result is

$$M_n^* = (m_e + m_h)/(1 - K_n/W),\qquad(1)$$

where m_e is the electron mass, m_h is the hole mass, K_n is the kinetic energy of the exciton with principal quantum number n, and W is the average of the electron and hole bandwidths.

In deriving Eq. (1) Mattis and Gallinar assumed that the band structure was described by a simple "cubium" model, so that the form of this equation may be different in a more realistic case, but the general principle embodied in this equation may still hold: The mass of the exciton is greater than the sum of the bare electron and hole masses in disagreement with the above effective-mass result. In the next paragraph we show how inelastic electron scattering can be used to test directly the prediction of Mattis and Gallinar.

In the effective-mass approximation the energies of the excitons formed are given by

$$E_{1k} = E_g + E_1 + \hbar^2 k^2/2M,\qquad(2)$$

where E_g, the energy gap between the conduction and valence bands, is the minimum energy needed to produce an unbound electron-hole pair. The energy E_1 of relative motion takes discrete negative values (bound states) and positive continuum values.

Dispersion of the exciton band is given by the third term in Eq. (2). In optical-absorption measurements the photon wave vector is small compared to the Brillouin-zone dimensions, so that light can only excite the $k = 0$ states of the exciton. Electron-energy-loss spectroscopy is an ideal experimental technique to study this dispersion since the momentum transferred in the scattering event can be varied independently of the energy loss and large values of k can be attained. By measurement of the energy-loss spectra of the exciton at different momentum transfers the dispersion of the exciton can be measured directly and the translational mass of the exciton determined. We present in this paper measurements of the dispersion of the excitons in CuCl and NaF which support the result of Mattis and Gallinar.

NaF and CuCl were chosen for several reasons. First they have face-centered-cubic structures. This is important if a comparison is to be made with the theory of Mattis and Gallinar, since their theory can only be applied easily to cubic structures. The excitons are formed in a direct allowed transition that can be modeled by the effective-mass theory. Band-structure calculations for these materials show that the conduction and valence bands are approximately parabolic and isotropic near the center of the zone and out to wave vectors measured in this experiment. Parabolicity of the bands is required if the effective-mass approximation is to apply. Isotropy is important because we use polycrystalline samples and therefore each measurement is an average over all directions at a given momentum transfer. With the energy resolution used in this experiment, it is important to have an exciton with a large binding energy if it is to be well resolved; NaF and CuCl having binding energies of 1.5 eV [2] and 180 meV,[3] respectively.

Transmission electron-energy-loss spectra of NaF and CuCl were measured at room temperature with a high-resolution 280-keV electron spectrometer. Details of the spectrometer have been given elsewhere.[4] By selecting the scattering angle, we can measure

energy-loss spectra as a function of the momentum transferred to the sample in the inelastic collision. In this experiment the energy and momentum resolutions were 0.12 eV and 0.1 Å^{-1}, respectively.

The electron scattering differential cross section, with respect to energy loss E and solid angle Ω, for excitation of an electron from an initial state $|i\rangle$ to a final state $|f\rangle$ is given by

$$d^2\sigma_{if}/dE\, d\Omega = (4/a_0 q^4)|\langle f|e^{i\mathbf{q}\cdot\mathbf{r}}|i\rangle|^2$$

$$\propto (1/q^2)\mathrm{Im}(-1/\epsilon),\tag{3}$$

where q is the momentum transfer and a_0 is the Bohr radius. The momentum is related to the scattering angle θ and the momentum of the incident beam by $q^2 = k^2(\theta^2 + \theta_e^2)$, where $\theta_e = \Delta E/2E_0$, E_0 is the kinetic energy of the beam, and $\epsilon(q,\omega)$ is the longitudinal dielectric response function of the solid, which for small momentum transfers is equivalent to the optical (transverse) response function.

The initial and final states of the exciton, $|i\rangle$ and $|f\rangle$, in Eq. (3) can be expressed in terms of a product of the exciton envelope function $F_{nk}(r)$ and single-particle states for a hole in the valence band and an electron in the conduction band. These single-particle states can be represented as Bloch wave functions.[5] The matrix element in Eq. (3) then reduces to

$$\langle f|e^{i\mathbf{q}\cdot\mathbf{r}}|i\rangle = \langle u_{k,c}|u_{k+q,v}\rangle F_n(\mathbf{r}).\tag{4}$$

In this work we use relatively small values of q. We assume therefore that $\langle u_{k,c}|u_{k+q,v}\rangle$ does not vary much with momentum transfer and any momentum dependence that this term has is neglected in the analysis given below.

Samples were prepared by the evaporation of 200 Å of CuCl and NaF onto 100-Å-thick self-supporting carbon films. Spectra were measured for a series of momentum transfers between 0.1 and 0.5 Å^{-1}. Spectra of the carbon substrates were also measured at the same energy and momentum transfers. The contribution due to the carbon substrate was then subtracted from each spectrum by normalization of the carbon spectrum to the total spectrum in the energy region below the exciton; i.e., we assume that the CuCl and NaF make no contribution to the spectrum in the transparent region. A series of spectra for CuCl with the background substracted are shown in Fig. 1.

To check our carbon subtraction we performed a Kramers-Kronig analysis of our data taken over an energy range of 2 to 120 eV at a momentum transfer of 0.1 Å^{-1} and compared our results to previous optical measurements with favorable results.

A nonlinear least-squares fit was made to the data with use of the following model based on the effective-mass approximation (EMA) which is a slight modification of Elliott's[6] treatment. The hydrogenic
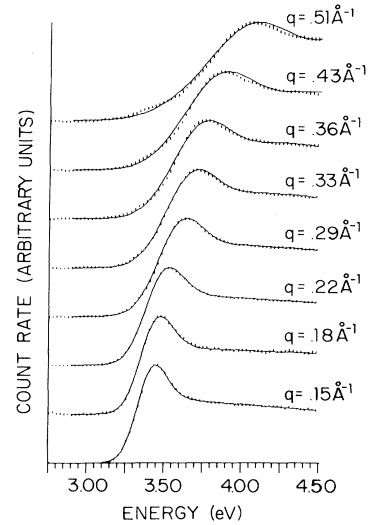

FIG. 1. Transmission electron-energy-loss spectra of CuCl at different momentum transfers. Dots, experiment; solid line, fit obtained with use of the model described in the text.

bound states are represented by a series of Gaussian peaks. The nth peak is located at an energy $E_n = E_g - E_b/n^2$, with an intensity that is $1/n^3$ of the $n = 1$ peak. E_b is the binding energy and E_g is the continuum threshold or true band gap. The lines are all assumed to have the same width σ. The EMA predicts a quasicontinuum formed by the discrete hydrogenic series as n approaches infinity that connects smoothly with the true continuum that starts at E_g. The continuum threshold does not appear as a distinctive feature in the data and so we treat E_g as a variable parameter in our model. We model the spectrum above the threshold energy by a step function at E_g with amplitude S and a straight line of slope m passing through E_g convoluted with a Gaussian line shape. The Gaussian is assumed to have the same width as the peaks used to model the bound states. This assumption is reasonable since the width is due to instrumental and phonon broadening, the first of which is certainly and the second likely to be the same for both the bound and the continuum states.

The CuCl exciton has a radius of 7.03 Å.[3] This is larger than the Cu-Cl bond length of 2.354 Å (only 15% of the charge is within the Cu-Cl bond length), so that the treatment of it as a Wannier exciton is fairly well justified. In NaF the $n = 1$ exciton has a radius that is approximately half of the alkali-halogen bond length and the Wannier model fails. It is possible, however, to modify the simple Wannier-Mott model to make corrections for the fact that the $n = 1$ exciton is tightly bound and approximately unscreened by the surrounding atoms.[7] In our model we include dielectric screening only for the discrete states with $n \geq 2$.

The data at each momentum transfer were fitted over the energy ranges 2.9 to 4.8 eV for CuCl and 9.6 to 14.0 eV for NaF, with this model. The results of this fitting procedure for CuCl are shown as solid lines in Fig. 1. The reduced χ^2 for each fit was typically 1.5, the worst case being a χ^2 of ~ 7 for the 0.5-Å^{-1} NaF data.

It is a simple geometry problem to show that the continuum threshold energy moves upward with q with an effective mass equal to $m_e + m_h$. Therefore, by locating both the exciton peak and the continuum threshold for a range of momentum transfers, we can directly measure $m_e + m_h$ and M^*. Figure 2 shows the dispersion of the exciton peak and the threshold energy for both samples. The solid lines are the results of a linear least-squares fit to the data. The fact that the exciton and continuum slopes are different shows that the exciton mass M^* is different from the effective mass of a noninteracting electron-hole pair in the same bands, as predicted by Mattis and Gallinar.

What is the physical origin of this mass difference? Two elements appear to be necessary for this effect to occur. The first is the nonparabolicity of the exciton energy as a function of momentum. Over the range of momenta included in Fig. 2 the energy is clearly parabolic. At higher momenta, however, the data fall below the straight lines drawn and become horizontal at the zone boundary. If the energy were parabolic for all values of q, Galilean invariance would apply and no mass difference would exist.

The second necessary element is the width of the exciton wave function in momentum speace as pointed out by Egri.[8] When an exciton is created near $q = 0$

the center of the wave function is in the parabolic part of the excitation curve. The wave function tails, however, reach out to the nonparabolic regions, giving rise to the mass difference.

From the dispersion curves the following effective masses are obtained: $(3.6 \pm 0.3)m_0$ for the exciton mass and $(2.4 \pm 0.3)m_0$ for the sum of the effective electron and hole masses in NaF. For CuCl we obtain $(1.23 \pm 0.03)m_0$ and $(0.83 \pm 0.03)m_0$ for these masses.

We now compare these results with what is expected from Eq. (1). The exciton binding energy E_b can be decomposed into kinetic K and potential energy V,[1] $E_b = -(K + V) \geqslant 0$. In the case of the Coulomb potential in the EMA limit, K is related to V by the virial theorem: $K = -\frac{1}{2}V$. Using this theorem and our measured values of the masses we can calculate the value of the parameter W in Eq. (1). We obtain values of ~ 5.0 and ~ 0.6 eV for NaF and CuCl, respectively. Photoemission experiments[9] on NaF give a value of 4.9 eV for the width of the valence band. Assuming approximately the same width for the conduction band gives good agreement with the value that we determine here. Theoretical calculations of the valence bandwidth in NaF give values that vary from 0.7 eV, in a linear combination of atomic orbitals calculation,[10] to 3.4 eV in a tight-binding calculation.[11] For CuCl our value of 0.6 eV is smaller than the typical value of ~ 2.0 eV obtained from band-structure calculations[12, 13] and photoemission experiments.[14] Stated simply, our observed mass difference is about what is expected for NaF, but is greater than that predicted by Eq. (1) for CuCl.

Our value of $1.23m_0$ for the translational mass of the CuCl exciton agrees well with a value obtained from a measurement of the wavelength shift of the exciton absorption line as a function of the CuCl microcrystallite size.[15] Apart from this experiment our result is in strong disagreement with other measurements. These experiments may be divided into two groups: direct determinations of the exciton mass and indirect or model-dependent measurements. An experiment that directly determined the mass is a two-photon Raman measurement[16] at 1.6 K that measured the dispersion of the longitudinal and transverse excitons out to 0.06 Å^{-1} and determined masses of $3.14m_0$ and $2.3m_0$ for the longitudinal and transverse masses, respectively.

Indirect determinations of the exciton mass have been obtained by the measurement of exciton–free-electron interactions[17] and exciton-exciton interactions[18] and from the modeling of the hyperfine contributions to the exciton absorption spectrum with a nonhydrogenic model.[3] These experiments give electron masses of $0.43m_0$, $0.44m_0$, and $0.415m_0$, respectively, and hole masses of $4.2m_0$, $3.6m_0$, and $20m_0$, respectively. All of these experiments are performed
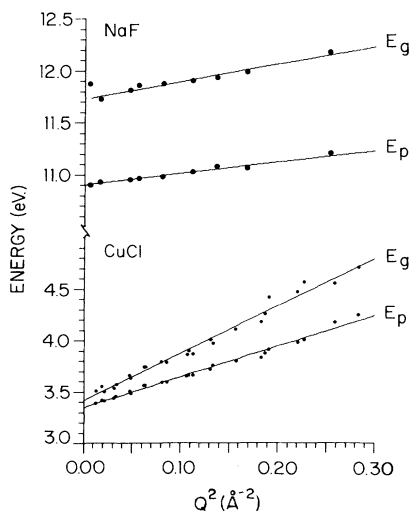
FIG. 2. Dispersion of the exciton peak, E_p, and continuum energy, E_g, for CuCl and NaF. Dots, experiment; solid line, linear fit to the data. Calculated and experimental errors are smaller than the dot size.

at energies that are less than or comparable to the energy of the LO phonon ($\hbar\omega_0 = 27$ meV) in CuCl. In our experiment we create excitons much higher above the zone-center minimum than the LO phonon energy. Our mass is therefore free of polaron-coupling effects.

If we assume that our measurement gives a value for the bare exciton mass whereas previous experiments measure a polaron mass then it is possible to evaluate the exciton-polaron coupling constant. Taking the bare exciton mass as $1.23m_0$ and the coupled mass to be $3.14m_0$, and assuming the simplest form for the coupling, $M^* = M(1 + \alpha/6)$, gives a value of 9.3 for α. This is the first direct measurement of the polaron coupling constant for an exciton, as opposed to a free electron or hole.

In a small exciton the polarization clouds of the electron and hole tend to neutralize each other,[19] so that the calculated polaron mass of the exciton is less than the sum of the free electron and hole polaron masses. Upon the assumption that the electron does not couple to the phonons, this gives a lower limit of 9.3 for the coupling constant of the free hole.

Kleinman and Mednick[12] made a self-consistent band-structure calculation of CuCl and have calculated the effective band masses. For the conduction band they obtain a value of $0.417m_0$, in good agreement with experiments. This calculation gives hole masses of $1.477m_0$ and $(0.969-3.101)m_0$. These values indicate that, as they suggested, the electron does not form a polaron in CuCl while the hole does. With the assumption of an electron mass of $0.42m_0$, our measurements indicate a hole mass of $0.42m_0$, considerably smaller than the predicted value.

Several points about the method of analysis of the data require further discussion. The data were fitted with a model based on the EMA. Even though good fits to the data were obtained, one can question whether this is the most accurate model to describe these excitons. This model has been used by other authors[20] to analyze data in cases where the exciton is known to be of the Frenkel type. We use the model only to parametrize the data, in particular to locate the energies of the exciton and the continuum. The peak energies and therefore the exciton masses are model independent. Since there is no feature in the spectrum that clearly shows where the continuum energy is, its value is model dependent. However, using this model to fit the spectra obtained from the Kramers-Kronig analysis gives values of 1.4 ± 0.1 eV and 170 ± 10 meV for the NaF and CuCl exciton binding energies which agree with the accepted values of 1.5 eV and 180 meV, and so we feel confident that our determination of the

continuum energies is accurate and that their dispersions are indeed different from that of the exciton.

We have obtained preliminary data on three additional insulators which all show the Mattis-Gallinar effect. This appears to be a general property of excitons.

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