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Crystal Size Effects on the Exciton Absorption Spectrum of WSe_2

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The thickness dependence of the optical absorption spectrum of thin single crystals of WSe_2 (500 Å to a unit-cell layer) was studied in the wavelength region 8000–5000 Å at 77°K. A significant shift (0.15 eV) to higher energies in the position of the exciton absorption peaks was observed with decreasing thickness. Such a shift is shown to follow a $1/t^2$ dependence on the thickness (t) down to 40 Å. This fact suggests the presence of a quantum size effect. A deviation from the $1/t^2$ law has been observed for crystals less than 40 Å thick.

INTRODUCTION

Quantum size effects should be observable in thin crystals when the thickness is sufficiently reduced. From uncertainty principle arguments, the energy gap of a semiconductor should increase as $1/t^2$, where t is the crystal thickness.[1] Similarly, the exciton absorption energy should ultimately shift with a $1/t^2$ dependence as the thickness is reduced.[2] Such quantum effects may be masked in thin films because of imperfections in both the crystal structure and the surfaces.

The semiconducting layer structures, such as MoS_2, WSe_2, and other related compounds are ideal candidates for such experiments, since crystals can be successively cleaved down to thicknesses of a few unit-cell layers.[3,4] For a comprehensive summary of the optical absorption and crystal structure of WSe_2 and the other transition-metal dichalcogenide layer structures, the reader is referred to a review by Wilson and Yoffe.[5]

In this paper, we present the results of measurements on the exciton absorption of single crystals of WSe_2 in the thickness range 500 Å down to a unit-cell layer (13.0 Å).

CRYSTAL PREPARATION

Single crystal platelets of WSe_2 were grown by chemical vapor transport, following the methods described by Brixner.[6] The purity of the elements was 99.999% for the W and 99.9999% for the Se. The optical measurements reported below were carried out on thin crystals (less than 1000 Å thick) cleaved and mounted in four different ways: free crystals, crystals on fused quartz, on mica, and on Epoxy. The free crystals were cleaved from a thick crystal platelet using fine tweezers. They were usually found at the edge of a thicker crystal and typically had lateral dimensions of 0.1 mm or less. It was possible to obtain crystals down to thicknesses of about 400 Å using this method.

In order to obtain thinner crystals it was necessary to use a substrate. If a free crystal, cleaved as described above, was placed on a smooth substrate it was found that the crystal was held on the surface by strong surface forces. It was then possible to further reduce the thickness by peeling away part of the crystal. Crystals were prepared on substrates of fused quartz and mica down to a thickness of about 50 Å. Crystals were also prepared on various Epoxies. Here, a crystal of WSe_2 was bonded to a uniform layer of Epoxy. It was possible to reduce the thickness by simply peeling away the crystal with sticky tape. Crystals on Epoxy were by far the easiest to prepare. The thinnest crystals obtained were on Epoxy, their lateral dimensions were typically 0.1 mm or less. The Epoxy used in the measurements reported here was Aremco Crystalbond 509.

It is important that crystals on different substrates be studied, since the effects of crystal strain, usually introduced by the differential expansion of the crystal and the substrate, can be determined. It is apparent that a cooled crystal on quartz will be under tension and that a cooled crystal on Epoxy will be under compression.

CRYSTAL THICKNESS MEASUREMENTS

The optical transmission as a function of thickness for an absorbing film on a transparent substrate is a standard problem and is treated in a number of references.[7,8] If the absorption coefficient and the refractive index are known, it is possible to determine the thickness of a film from a measurement of the optical transmission.

We have measured the absorption coefficient α for thick WSe_2 crystals at a wavelength of 6000 Å (2.07 eV) and obtained a value of $(1.8\pm0.2)\times10^5\ \mathrm{cm}^{-1}$, at 77°K. Since the refractive index of WSe_2 has not been measured, we assumed a value of 3.5, based on measurements in the corresponding energy region between the absorption peaks A and B for MoS_2.[9]

It is well known that the optical constants of thin

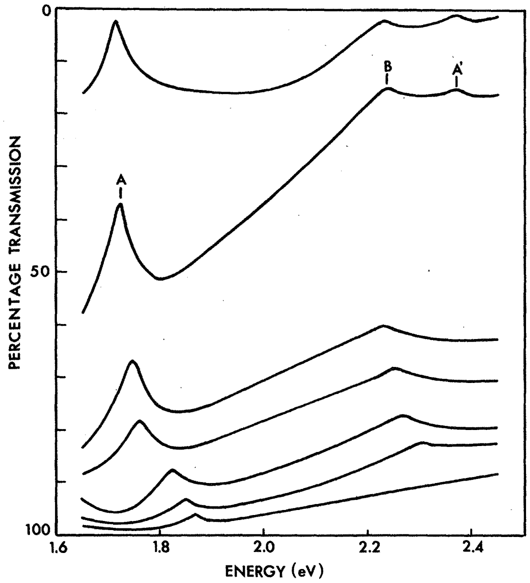

FIG. 1. Plot of the percentage transmission (T) against photon energy for WSe_2 crystals of decreasing thickness on an Epoxy substrate, at 77°K.

films are not necessarily the same as those for the bulk material, however, since the optical absorption spectrum for WSe_2 shows a consistency over a very large range of thickness, it seems reasonable to assume that the absorption coefficient and the refractive index remain essentially constant with thickness in energy regions away from absorption peaks (such as at 2.07 eV in Fig. 1). Thus we determined the thickness of a WSe_2 crystal by measuring the transmission at 2.07 eV and taking the crystal thickness from the theoretical plot of the transmission against thickness, using a value of 1.8×10^5 cm^{-1} for the absorption coefficient α and a value of 3.5 for the refractive index. A change in α of 10% results in a change in crystal thickness of approximately 8% in the thickness region between zero and 100 Å. Assuming α constant, a change in refractive index of 0.5 from 3.5 results in a change in crystal thickness of 20% in the thickness range zero to 100 Å.

Our thickness determinations gave some exceedingly small values such as 10 and 15 Å. Since the crystal thickness should be a multiple of 6.5 Å, the thickness of a molecular layer, we selected 13.0 and 19.5 Å for the above crystal thicknesses. Such small values are not unreasonable, since crystals of MoS_2 having such thicknesses have been prepared and measured using electron microscope techniques.[3]

OPTICAL ABSORPTION APPARATUS

A system was used which directly measured the optical transmission (I/I_0) of small crystals down to approximately 50 μ in lateral dimensions. In the optical system, light from a tungsten lamp passing through a spectrometer was focused onto a small crystal such that the light intensity was uniform over the crystal and areas adjacent to the crystal. A microscope objective lens was then used to focus an image of the crystal onto one of the two pinholes in front of a photomultiplier, and light from an area adjacent to the crystal was focused on the other pinhole. By means of a specially cut circular chopper blade, the light passing into the pinholes was modulated at different frequencies, namely, 40 and 100 Hz. The photomultiplier output was fed into two phase-sensitive detectors, one tuned to 40 Hz, the other to 100 Hz. The output from the detectors was fed into a divider, giving the ratio I/I_0. The output ratio I/I_0 was found to be insensitive to variations of 10% in both the tungsten lamp current and the photomultiplier voltage.

EXPERIMENTAL RESULTS

The optical absorption spectrum of WSe_2 in the wavelength region 8000 to 5000 Å was measured on a series of samples of decreasing thickness at 77°K. The most interesting features of the absorption spectrum in thick (2000 Å) free crystals are the exciton peaks A at 1.70 eV, A_2 at 1.74 eV, B at 2.18 eV, and A' at 2.26 eV. More general details of the spectrum can be found in the review by Wilson and Yoffe.[5] As the thickness of the crystals was reduced, several changes were observed in the spectrum as shown in Fig. 1. The most impressive change is given by the shift in the position of the A peak; a noticeable shift

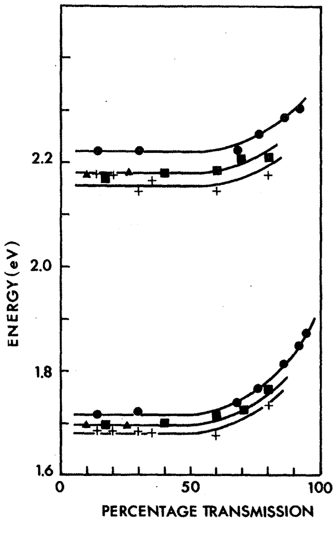

FIG. 2. Position of peaks A (lower curves) and B plotted against the percentage transmission for WSe_2 crystals at 2.07 eV (6000 Å), at 77°K. Free crystal, triangle; mica substrate, square; Epoxy substrate, circle; quartz substrate, plus.

of the B peak is also observed, while peak A' was not observed in the thinnest crystals.

Figure 2 shows the position of the A and B peaks from Fig. 1 plotted against the percentage transmission of the samples at 2.07 eV. The other curves relative to the same peak which appear in Fig. 2 were obtained using crystals on different substrates and give information about the effects of crystal strain.

The energy of peak A from Fig. 1 is plotted against $1/t^2$ in Fig. 3. The crystal thickness t was determined from the value of the transmission at 2.07 eV, as discussed earlier.

DISCUSSION

There are several factors that can influence the position of the excitonic peaks in the absorption spectrum of crystals and various models have been worked out theoretically in order to explain the experimental results.

The sets of curves for the A and B peaks in Fig. 2 can be explained in terms of the strain resulting from the differences in the thermal contraction of the crystals and the substrates. A comparison of the positions of the A and B peaks with free (unstrained) crystals in Fig. 2 shows that both A and B are shifted by strain. For crystals under tension (quartz substrate) the spectrum is shifted to lower energies; under compression (Epoxy substrate) the spectrum is shifted to higher energies. The peak positions for crystals on mica are not very different from those for free crystals. The similar shape and constant separation of the curves for crystals on different substrates indicates that the shift caused by strain is the same for all thicknesses. This fact implies that the shifts observed with decreasing thickness are not caused by strain.

We suggest that these shifts can be explained in terms of a crystal size effect. From a simple application of the uncertainty principle, a $1/t^2$ dependence of the energy of excitonic absorption has been predicted.[2] Similarly, the energy gap of a semiconductor has been predicted to increase by an amount[1]

$$\Delta E_g \approx \hbar^2/2mt^2. \tag{1}$$

If perfectly rigid boundary conditions are assumed at the film surfaces, Eq. (1) becomes[10]

$$\Delta E_g = \pi^2(\hbar^2/2mt^2), \tag{2}$$

where t is the film thickness and m is the reduced electron-hole effective mass,

$$1/m = 1/m_n + 1/m_p \tag{3}$$

and m_n, m_p are the electron and hole effective masses, respectively.

Our results are consistent with the quantum size effect predicted by Eq. (2) for film thicknesses greater than 40 Å. As shown in Fig. 3, the shift of the A peak is linear in $1/t^2$, down to a thickness of approximately 40 Å. If it is assumed that for this range of crystal thickness the exciton binding energy is approximately independent of thickness, then the shift of the A peak directly reflects the variation of bandgap with thickness and Eq. (2) may be used to interpret the data. In this manner, a fit of Eq. (2) to the data in Fig. 3 yields $m = 0.24 m_0$, where m_0 is the free electron mass.[11]

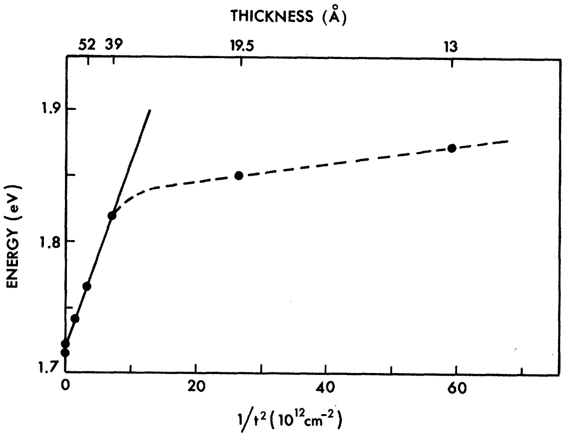

FIG. 3. Energy of peak A plotted against $1/t^2$, where t is the thickness, for WSe_2 crystals on an Epoxy substrate, at 77°K.

For thicknesses less than 40 Å the shift of the A peak with thickness is much weaker and cannot be accounted for by Eq. (2). We suggest that this is either due to the unrealistic nature of the boundary conditions used to derive Eq. (2) or to an increase of the exciton binding energy with decreasing thickness, or to a combination of these effects. An increase in exciton binding energy might be expected on the basis of a result by Ralph[12] which states that the binding energy of a truly two-dimensional exciton is four times the three-dimensional value. It is of interest to note that the deviation of the data in Fig. 3 from a $1/t^2$ dependence occurs at a thickness $t \approx 2a_1$, where a_1 is the exciton radius. Using the Mott-Wannier model, which works well for MoS_2 [9], and the position of the A_2 peak for a thick WSe_2 crystal, and a dielectric constant of 7 (appropriate for MoS_2 [9]) one obtains $a_1 = 21$ Å. It therefore appears likely that a complete theoretical account of the data will require a discussion of the dependence of exciton binding energy on film thickness. No such account is presently available for the range of film thicknesses covered by our experiments.

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Absolute Signs of Second-Harmonic Generation Coefficients of Piezoelectric Crystals

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This paper describes the measurement of the absolute signs of the nonlinear optical coefficients d_{ij} that give rise to second-harmonic generation in piezoelectric crystals. The measurements were made with a repetitively Q-switched Nd-yttrium aluminum garnet (Nd-YAG) laser (1.064 μ) and involve relative sign determinations between two crystals followed by a comparison of at least one of them with d_{14} of GaP, which has been shown previously to be positive with respect to the +[111]. To determine the unique directions in the crystals studied, several different methods were used, including: the piezoelectric effect, the pyroelectric effect, the etching behavior, and the electric field aligned spontaneous polarization. The crystals investigated included the following: zinc-blende crystals (ZnSe, ZnTe, and CdTe), wurtzite crystals (ZnO, BeO, CdS, and CdSe), ferroelectric crystals [$LiTaO_3$, $LiNbO_3$, $BaTiO_3$, $Ba_2NaNb_5O_{15}$, $Gd_2(MoO_4)_3$, and $Tb_2(MoO_4)_3$], and several other crystals ($LiIO_3$, $LiGaO_2$, $LiCHO_2 \cdot H_2O$, and quartz). Strong absorption of the second harmonic complicates the interpretation of the experimental results for ZnTe, CdTe, and CdSe. The present results and those of several recent theoretical predictions are in good agreement.

I. INTRODUCTION

Recently, there have been a number of useful calculations of the signs and/or the magnitudes of the nonlinear optical coefficients d_{ij} that describe second-harmonic generation (SHG) and optical parametric interactions in piezoelectric crystals. One of the more important earlier predictions,[1,2] which was for crystals with wurtzite (w) and zinc-blende (z) structures, was that

$$d_{33}(w) = -2d_{31}(w) = (2/\sqrt{3})\, d_{14}(z).$$

Of the several papers that have considered SHG with III–V compounds,[2–5] the most successful utilized the electrodynamical bond-charge model,[2] which led to predictions of signs and magnitudes in good agreement with experiment. In the case of the II–VI compounds, the bond-charge model, modified to take into account unequal atomic radii,[6] was even able to account for the observed[7] sign reversal of the d's in going from CdS to ZnO. Other publications have included predictions for several of the niobates,[8] HIO_3 and $LiIO_3$,[9] quartz,[6] and the general class of polar crystals.[10]

The early work having to do with sign predictions, notably that of Levine,[2] and Jeggo and Boyd,[8] stimulated the present rather extensive experimental investigation aimed at determining the absolute signs of the d's for a variety of different crystals. Prior to the present measurements, the only published determinations of the absolute signs of d's were for several crystals with the zinc-blende structure, namely, GaP,[11] and GaAs, InAs, and GaSb.[12] Some of the present results have been described previously in abbreviated letter form[7]; however, this paper presents a detailed description of the experimental measurements and many heretofore unpublished results.

The magnitudes of the d's were not, in general, determined during the course of this study since they had been measured previously for most of the crystals investigated, and the results are included in an excellent recent summary of experimental data.[13]

II. DETERMINATION OF UNIQUE CRYSTALLINE DIRECTIONS

The absolute signs of d only have meaning when they are related to an absolute direction in the piezoelectric