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2000 J. Phys.: Condens. Matter 12 6719

(http://iopscience.iop.org/0953-8984/12/30/304)

J. Phys.: Condens. Matter **12** (2000) 6719–6723. Printed in the UK PII: S0953-8984(00)14053-6

Exciton absorption spectra of MoS_2 crystals in high magnetic fields up to 150 T

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Received 19 May 2000

Abstract. We have measured the absorption spectra of a cleaned MoS_2 natural crystal in high magnetic fields up to 150 T in a Faraday configuration, and we have found Zeeman splitting and a diamagnetic shift of the $n = 1$ A exciton band. The g-factor and the diamagnetic parameter are calculated to be -4.6 and 1.8×10^{-4} meV T^{-2}, respectively.

1. Introduction

An MoS_2 crystal is an indirect-band-gap semiconductor and there appears a very weak absorption starting from 1.24 eV in the infrared region [1]. Very strong absorption bands are observed in the visible region due to dipole-allowed excitons [2]. This crystal has a layer-type crystal structure and can be sliced into extremely thin films, with thickness less than the Bohr radius of the higher-order exciton. Using this technique, the quantum size effect has been studied and summarized by Evans and Young [3] in the early stages of an extensive investigation of size quantization. According to band-structure calculations carried out by Coehoorn and Haas [4], two strong exciton bands named A and B in order from the lower-energy side correspond to K_4-to-K_5 and K_1-to-K_5 transitions, respectively, at the K point of the Brillouin zone. The K_4–K_1 splitting in the valence band is due to both interlayer interaction and spin–orbit splitting of the d orbital of Mo.

First, Evans and Young [5] found diamagnetic shifts of the A_n ($n \geqslant 2$) excitons in weak magnetic fields up to 2.78 T. Neville and Evans [6] found Zeeman splitting of the $n = 1$ A exciton, A_1, as well as diamagnetic shifts of the A_n ($n \geqslant 2$) exciton lines in magnetic fields up to 10.2 T, and the absolute g-value was calculated to be 7.5 ± 1 for the A_1 exciton. Tanaka *et al* [7] measured the magnetic circular dichroism and reported an effective g-value of -3.1 ± 0.1 for the A_1 exciton.

Thus, previously reported g-values are very different from each other, and, to the best of our knowledge, there has been no report on a diamagnetic shift of the A_1 exciton. The g-value and the diamagnetic shift have provided important information on the spin–orbit interaction and the internal motion of the exciton, respectively. In this paper, we describe the absorption spectrum of the A-exciton region in high magnetic fields up to 150 T, and we obtain the g-value and the diamagnetic parameter of the A_1 exciton.

0953-8984/00/306719+05$30.00

2. Experimental procedure

A very thin crystal of MoS_2 was peeled off with transparent adhesive tape from a large natural crystal mined in Japan. The crystal thickness was estimated to be 0.4 μm from the interference spectrum, and the crystal optical axis was normal to the crystal surface. The thin crystal with the adhesive tape was set on the edge of a sample holder in a helium-gas-flow-type cryostat designed for high-field magnetization measurements [8].

High magnetic fields up to 150 T with a pulse width of $\sim$7 μs were generated by the single-turn coil method. The time-resolved two-dimensional spectra were measured using a streak spectrometer consisting of an image-converter camera and a CCD camera, the details of which were reported previously [9].

The temperature of the helium gas around the sample was 25 K and the error of the magnetic field was less than 1.5%. The absorption spectra were measured using circularly polarized light in the Faraday configuration, and the spectral resolution was 1.2 nm.

3. Experimental results and discussion

Figures 1 and 2 show the absorption spectra in several magnetic fields up to 150 T in the σ^+- and σ^--polarizations, respectively, at 25 K.

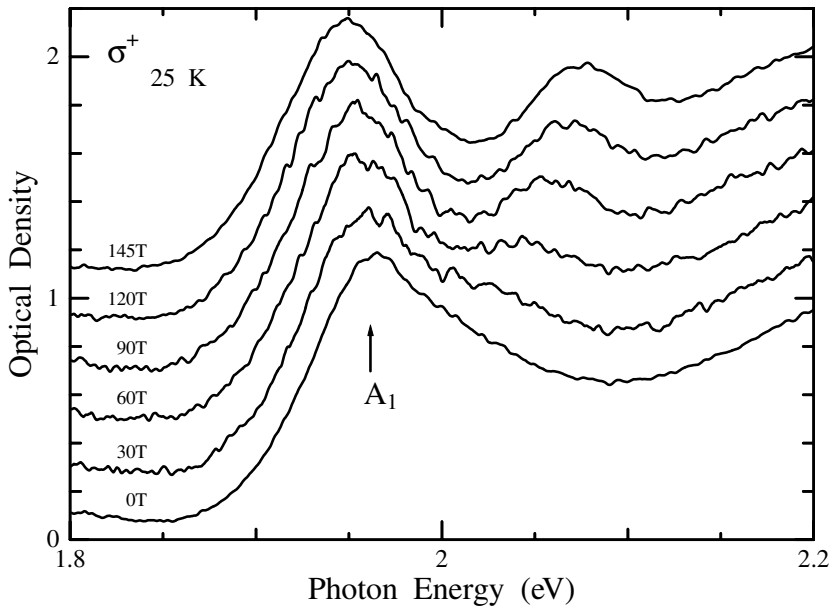

Figure 1. Absorption spectra in different magnetic fields for σ^+-polarized light in a Faraday configuration at 25 K.

The absorption peak at 1.96 eV in zero magnetic field is associated with an A_1 exciton. Peaks due to higher-excited-state excitons A_n ($n = 2, 3, 4, \ldots$) could not be observed, probably because of the strain in the thin crystal. The band A_1 in figure 1 for the σ^+-polarization shifts to the lower-energy side with increases in the magnetic field. The A_1 band has an asymmetric shape with a higher-energy tail. In the less-strained crystal, there appears a sub-band on the higher-energy side of the A_1 band, and the energy of this sub-band is located near the A_n

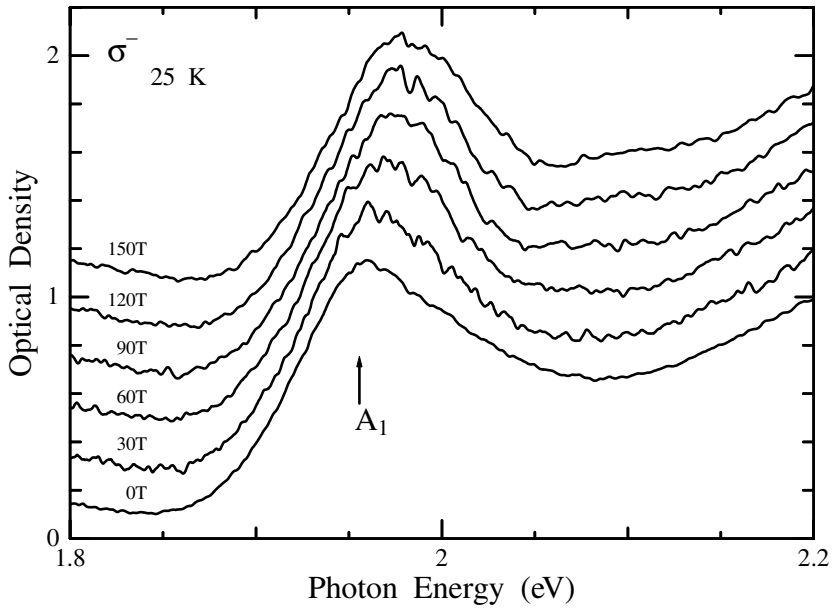

Figure 2. Absorption spectra in different magnetic fields for σ^--polarized light in a Faraday configuration at 25 K.

($n = 2, 3, 4, \ldots$) bands, which were found by Evans and Young [2]. Hence, this asymmetry of the A_1 band may be associated with the higher excited states of the A exciton. When the magnetic field increases, a new band appears on the higher-energy side of the A_1 band and grows gradually. This new band might be related to the excited states of the A exciton, but the origin of the growth is not clear at present. Peak A_1 in figure 2 for the σ^--polarization is shifted substantially to the higher-energy side as the magnetic field becomes larger, and the higher-energy shoulder does not seem to be shifted and merged into the A_1 band.

In figure 3, the peak energy of the A_1 exciton band is shown as a function of the magnetic field H for σ^+- and σ^--polarizations by closed and open circles, respectively.

Wheeler and Dimmock [10] calculated the $n = 1$ exciton energy of uniaxial crystals in a magnetic field using an effective-mass approximation. For a circularly polarized light incident normal to the cleaved crystal surface in a Faraday configuration, the $n = 1$ exciton energy $E(H)$ as a function of H is expressed as

$$E(H) = E_0 \pm \frac{1}{2}\beta_0(g_{hz} - g_{ez})H + \sigma_z H^2. \tag{1}$$

The diamagnetic parameter σ_z is written as

$$\sigma_z = \frac{1}{4}\frac{e^2}{m_0 c^2} a_0^2 \frac{1}{\mu_\perp^3}\varepsilon_\perp \varepsilon_\parallel \tag{2}$$

where E_0 is the exciton energy without a magnetic field, β_0 is the Bohr magneton, g_{hz} and g_{ez} are the g-factors of the electron and the hole, respectively, e is the electron charge, m_0 is the free-electron mass, c is the velocity of light, a_0 is the Bohr radius of the hydrogen atom, $\mu_\perp$ is the effective reduced mass on the surface perpendicular to the c-axis, and $\varepsilon_\perp$ and $\varepsilon_\parallel$ are effective dielectric constants perpendicular and parallel to the c-axis, respectively. The second and third terms of equation (1) represent the paramagnetic Zeeman splitting and the diamagnetic shift, respectively. Dotted lines show the results of calculations using equation (1)

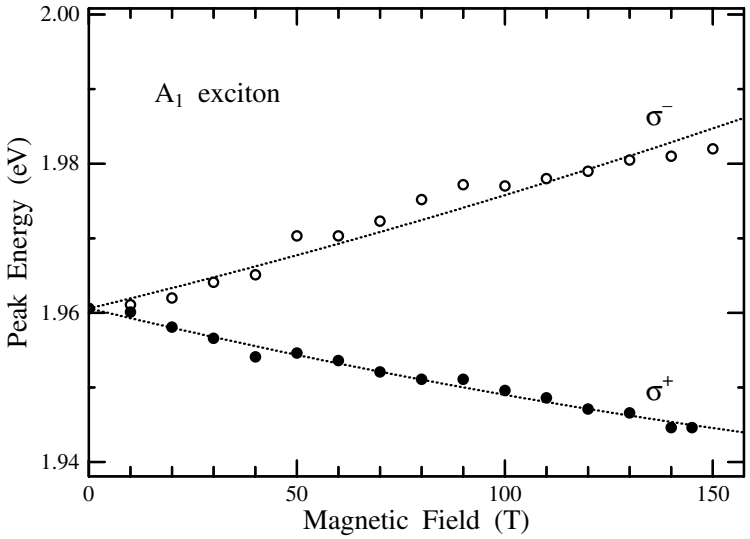

Figure 3. A_1-exciton peak energy versus the magnetic field. Closed and open circles show the measured energies for σ^+- and σ^--polarized light, respectively. Dotted lines represent the calculated curves obtained using equation (1).

with adjustable parameters $g_z = g_{hz} - g_{ez} = -4.6$ and $\sigma_z = 1.8 \times 10^{-4}$ meV T^{-2}. In figure 4, the diamagnetic shift is shown by open circles, and the calculated energy shift is shown by a dotted line. The experimental points in figures 3 and 4 agree well with the calculated curves.

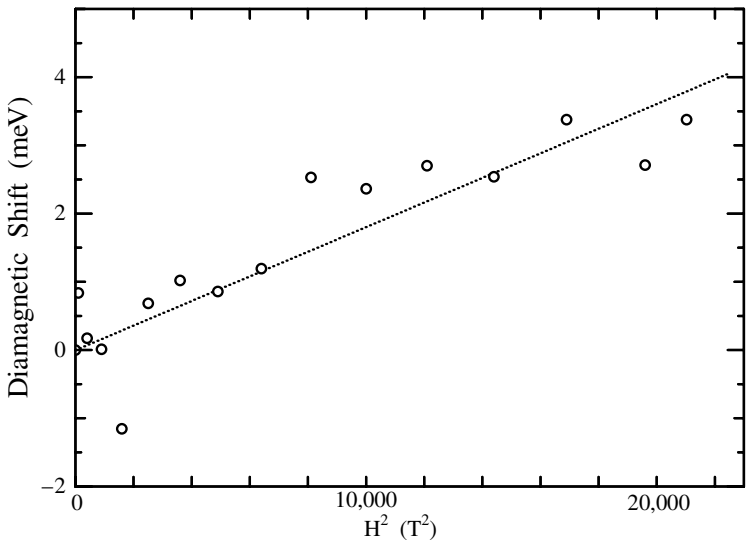

Figure 4. Diamagnetic shift versus the square of the magnetic field. Open circles show the experimental data and the dotted line represents the calculated diamagnetic field.

From equation (2), the effective reduced mass perpendicular to the c-axis, $\mu_\perp$, is calculated to be $0.40 \pm 0.02\ m_0$ using $\varepsilon_\perp = 20.16$ and $\varepsilon_\parallel = 4.80$ [6]. The binding energy $R_\perp$ and the Bohr radius $r_\perp$ of the A_1 exciton in the plane perpendicular to the c-axis are estimated to be

56 ± 2 meV and 1.28 ± 0.04 nm, respectively, using the following equations:

$$R_\perp = R_y \frac{\mu_\perp}{\varepsilon_\perp \varepsilon_\parallel} \tag{3}$$

$$r_\perp = a_0 \frac{\sqrt{\varepsilon_\perp \varepsilon_\parallel}}{\mu_\perp} \tag{4}$$

where R_y is the binding energy of a hydrogen atom.

The binding energy $R_\perp$ obtained is a little larger than the energy 45 meV [3] estimated from the Rydberg series of A-exciton energies. The exciton Bohr radius obtained in close to the radius 1.4 nm estimated from the Rydberg series [6], but is slightly larger than the calculated value of 0.95 nm [11].

The g-factor of -4.6 is close to the value of -3.1 obtained from magnetic circular dichroism by Tanaka *et al* [7], but it is smaller than the value 7.5 obtained by Neville and Evans [6]. All the estimated values relating to the A_1 exciton are listed in table 1.

Table 1. Parameters for the A_1 exciton.

g-factor (g_z)	-4.6 ± 0.08
Diamagnetic shift (σ_z)	$(1.8 \pm 0.15) \times 10^{-4}$ meV T^{-2}
Reduced mass ($\mu_\perp$)	$0.40 \pm 0.02\ m_0$
Binding energy ($R_\perp$)	56 ± 2 meV
Bohr radius ($r_\perp$)	1.28 ± 0.04 nm

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