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Excitons in molybdenum disulphide

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Optical spectra of MoS_2 in the excitonic region were obtained by photoconductivity, photovoltaic effect and wavelength-modulated reflectivity at temperatures of 300 to 4.2 K and in magnetic fields of up to 70 kG. Cleaved natural crystals and synthetic crystals studied in both the Faraday and Voigt configurations showed nearly the same characteristics. The results indicate the possibility of up to four excitonic series in MoS_2 as in other Mo dichalcogenides, and support band-structure calculations predicting flat conduction and valence bands originating from Mo orbitals. A ground-state anomaly of the A exciton is explained by a central cell correction of the type used by Harbeke and Tosatti to explain a similiar anomaly in PbI_2. The reduced mass of the A exciton is found to be $\mu^* \simeq 0.4m_0$, both from the study of the series itself, and from its magneto-optical properties, thus removing a large discrepancy found in previous work.

I. INTRODUCTION

Molybdenum disulphide (MoS_2) is a member of a family of layered compounds of the transition-metal dichalcogenides well known chemically and structurally[1]; its fundamental optical properties[2-5] and its band structure[6-9] have been extensively studied. Optically, MoS_2 has been the subject of much interest for the structures appearing in the absorption,[10, 11] photovoltaic,[12] photoconductivity,[13] reflectivity,[4, 14] and magnetoabsorption[15] spectra. The structures are generally attributed to the existence of two excitonic series A and B characterized by fundamental levels still evident at room temperature; the higher excitonic levels, however, are not unequivocally identified by the different authors.

Two kinds of band-structure calculations are at present available for MoS_2: a tight-binding calculation, performed by Edmondson[6] and Bromley *et al.*,[7] and *ab initio* calculations made by Mattheis[8] with an augmented-plane-wave (APW) method and by Kasowski[9] with a "muffin-tin-orbitals" method. All calculations predict the same band sequence at Γ; the calculated energy separations between the bands are, however, different so that different assignments are given for the structures A and B. In the Mattheis and the Kasowski band calculations, the A and B structures are assigned to transitions from a molybdenum d_{z^2} valence band to a spin-orbit-split conduction band originating from the other molybdenum d orbitals. In the tight-binding computation, the d_{z^2} band is very narrow and it lies inside the gap; A and B transitions thus come from an underlying p-like valence band (originating from sulphur orbitals) to a d-like conduction band, the same as for the case of the *ab initio* band structure. The hole wave function is therefore different in the two models and a knowledge of the exciton parameters would allow a useful check. Nevertheless none of the above band structures can be said, at present, to give a better account of the optical properties in the excitonic region. Indeed in spite of the large number of studies, excitons in MoS_2 are still not sufficiently understood.

The first observation of excitons in MoS_2 is due to Frindt and Yoffe[10] (FY), who found at 4.2 K a series of three bands (A_1, A_2, A_3) interpreted, on the basis of their position and their oscillator strength, as resulting from the formation of Mott-Wannier unlocalized excitons; a similar assumption was made for another band, B, not showing any structure. The exciton parameters were not derived by FY; only a rough evaluation of excitonic radii are given. A more complex structure was found at 77 K by Evans and Young[11, 15] (EY) both for A and B bands (A_1 to A_6 and B_1 to B_4). From an analysis of this structure on the basis of the effective-mass approximation as well as from magneto-absorption studies (up to 25 kG), the authors could deduce the exciton parameters; unfortunately the electron effective masses deduced from both methods differ by a large factor. In addition, the structures found by EY were not confirmed by further studies under the same,[16] or better,[17-19] experimental conditions. It thus appears that the effective mass is still unknown for MoS_2.

The present work is a detailed analysis of the excitonic region of MoS_2 spectra obtained at different temperatures from 300 K down to 4.2 K and in magnetic fields of up to 70 kG. Extending the measurements to lower temperatures, it was hoped, could better resolve the spectra, while the use of high magnetic fields could help clarify the abovementioned effective-mass discrepancy. The spectra were obtained by several different techniques. Preliminary investigations of the photoelectromagnetic (PEM) effect at low temperatures and in high magnetic fields were not very successful because of low signal-to-noise ratios. Better results were obtained for the photoconductivity (PC) and the photovoltaic (PV) effect and especially for the wavelength-modulated reflectivity (WMR). It was accordingly decided to make most use of this last technique. Wavelength modulation has been shown through numerous studies[19,20] to enhance the visibility of the spectral structures, while removing the need for thin crystals necessary for the detection of excitons in absorption spectra, and thus avoiding at the same time the so-called confinement effect[21] and the shift of the spectral structures arising from the difference in thermal expansion of the crystal and the substrate.[10]

The paper first gives an outline of the experimental method used and then presents the results of the wavelength-modulated reflectivity (at 4.2 K) without magnetic field. A comparison is made with PC spectra. A study of the position, width, and relative amplitude of the spectral peaks as a function of the temperature is then presented and discussed in order to understand the nature of the transitions; the effect of the magnetic field on the spectra at 4.2 K is then considered. Section IV deals with the relevance of the present results to the band structure of MoS_2.

II. EXPERIMENTAL

In order to check the effect of the sample origin on the spectra, two types of crystals were investigated: natural samples cleaved from large crystals originating from the ancient Sarroch mine of Sardinia, and synthetic crystals grown by vapor iodine transport by J. Brebner of the University of Montreal. Both types of crystals belong to the $2H$ polytype. Samples were thick enough (>1 μm) to give spectral structures independent of thickness. Spectra were taken on the natural face normal to the hexagonal C axis. It may be said immediately that within experimental error, the position of the spectral structures is the same in both types of crystals; in the natural crystals, however, the structures are slightly sharper and accordingly, results presented below deal mostly with natural crystals.

The optical system consisted of an ordinary tungsten lamp (quartz-iodine lamps give spurious structures in WMR spectra) coupled to a $\frac{3}{4}$-m Czerney-Turner Spex monochromator. The wavelength modulation was provided by a refractor plate mounted on an asymmetric cam driven synchronously at 12 Hz, and providing a modulation amplitude of about 10 Å, corresponding to $\frac{1}{3}$ of the mean width of the structure studied. The modulation assembly was located inside the monochromator near the entrance slit.

The monochromatic beam was focused on any of seven samples of MoS_2 mounted strain free in either the Faraday or Voigt configuration within the region of high-field homogeneity (±0.5%) of a superconducting magnet. The magnet, which can provide fields of up to 72.5 kG, is mounted horizontally in a cryostat equipped with an independent sample chamber that can be filled with He exchange gas at low pressure. CaF_2 was used for the room-temperature window and sapphire for the cold window. Light reflected from a sample was focused on to the entrance slit of a $S1$ response photomultiplier (PM) situated at a distance of 1 m from the solenoid; at such distance, the effects of the magnetic field on the PM response are negligible. Amplification and detection of the signal from the PM was performed with a lock-in amplifier (PAR model No. 220) synchronized by a 12-Hz reference from the modulation system. PC and PV spectra were carried out in the same experimental arrangement: the wavelength was not modulated but the light was chopped at 85 Hz and the signal detected by an ordinary synchronous system.

III. RESULTS AND DISCUSSION

A. Spectra at 4.2 K in zero magnetic field

In Fig. 1 typical WMR and PC spectra of MoS_2 taken at 4.2 K on natural samples are shown together. The PV spectrum (not shown) was nearly identical to the PC spectrum. A common feature of those spectra is that the WMR and PC minima occur at nearly the same wavelength. In Table I the position of the WMR and PC minima are compared to the position of the maxima in the absorption spectra obtained at the same temperature by different authors[10,18]; the best agreement is found with the FY[10] results (freely mounted samples). The above correspondence is not a general feature in exciton spectra but it is related to the value of the optical constants of the material.

Excitonic transitions are generally interpreted as resonances in the optical constants ϵ_1, ϵ_2:

$$\epsilon_1 = n_\infty^2 + \frac{f(\omega_0 - \omega)}{(\omega_0 - \omega)^2 + g^2},$$

$$\epsilon_2 = \frac{1}{2}\frac{f}{(\omega_0 - \omega)^2 + g^2}, \qquad (1)$$

where f is the oscillator strength, g is the damping constant, related to the half-width of the spectral line, and n_∞ is the value of the refractive index without the excitonic contribution. It may easily be shown that when the attenuation index k is small with respect to the refractive index n, the reflectivity R reproduces with sufficient fidelity ϵ_1 and the absorption reproduces ϵ_2; the absorption is then peaked at $\omega = \omega_0$, whereas for the same frequency, R shows an inflection point seen as a minimum in a derivative spectrum. The values of n and k are known for MoS_2 in all the spectral range where excitons are detected[10, 11] and these values allow the above assumption. The minima shown in the WMR spectrum thus correspond to maxima in ϵ_2 and maxima in the absorption spectrum.

The PC spectrum of Fig. 1 is a typical "negative" spectrum as excitonic transitions are related to a fall of the photoresponse; other samples having the same apparent physical characteristics displayed in the same conditions "positive" spectra with maxima located near the energy of the absorption peaks. A similar behavior has often been observed in other semiconductors such as[22] CdS or[23] CdSe; samples of these materials are classified as type I when they exhibit "positive" PC spectra and as type II when they exhibit "negative" spectra. The type of photoconduction may be related to equilibrium between the carrier surface recombination generating a fall in the photoconductivity when the absorption coefficient increases,[24] and to the mechanism of exciton ionization producing a rise of the PC response near an excitonic transition. A good correspondence between exciton absorption and photocurrent peaks (either maxima *or* minima) was indeed found in many semiconductors[23-25]; the present correspondence between the structures appearing in absorption, PC, and WMR spectra therefore is not accidental and many types of spectra can thus be used to investigate the excitons in MoS_2. A first assignment for the structures of Fig. 1 can then be given.

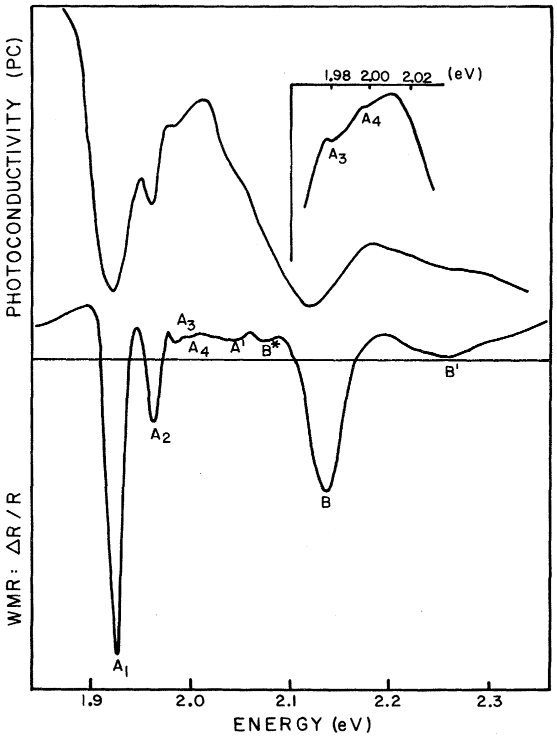

FIG. 1. Photoconductivity and wavelength-modulated reflectivity spectra at 4.2 K. The insert shows in more details the photoconductivity spectrum in the region of the A_3 and A_4 structures.

TABLE I. Comparison between the position of the peaks observed in MoS_2 with different techniques.

	Present work WMR (eV)	Present work PC (eV)	Absorption (eV)	Absorption Reference
A_1	1.9255	1.920	1.910	BKL (18)
A_2	1.9625	1.960	1.965	FY (10)
A_3	1.986	1.983	1.991	FY (10)
A_4	1.999	1.999	1.998	FY (10)
A'	2.040	2.036		
$B*$	2.073	···	2.057	BKL (18)
B	2.137	2.124	2.112	BKL (18)
B'	2.250	2.245	···	

Peaks A_1, A_2, A_3 seem to correspond to the first three levels of an excitonic series; A_4, observed both in PC and WMR spectra, is a very weak shoulder that could be the fourth level of the series; these peaks will be studied with more attention later on. Peaks B and B' will also be examined later to determine if they belong to another excitonic series. Peak B^* corresponds in energy to peak B in $3R$ samples[18] and is clearly evident only in synthetic crystals, whereas in the natural ones it is only sometimes detectable as a weak shoulder; this implies an appreciable $3R$ phase content in the synthetic material, a common occurrence according to Ref. 1. Peak A', also found at 77 K by Weiser[19] in a WMR spectrum, has not received any assignment up to now.

B. Temperature dependence

Figure 2 shows some WMR spectra of a natural crystal taken at different temperatures. The structures are both broadened and shifted as the temperature increases. In addition, A_3 has disappeared in the 160-K spectrum. Figure 2 allows a comparison with the spectra obtained by several atuhors at different temperatures. Good agreement is always found with the FY results; also the Weiser spectra[19] carried out at 77 K are perfectly reproduced at the same temperature.

The temperature dependence of the spectral position of all the observed peaks is shown in Fig. 3. All structures shift with temperature and within experimental error the temperature coefficient is identical for all the peaks, going from a nearly null value at 4.2 K to -3.5×10^{-4} eV/K at 300 K. Most semiconductors show a similar behavior, which was theoretically interpreted by Fan,[26] on the grounds of carrier-lattice interaction. A fitting of the present results to the theory of Fan is nevertheless not possible, since several parameters are still unknown for MoS_2.

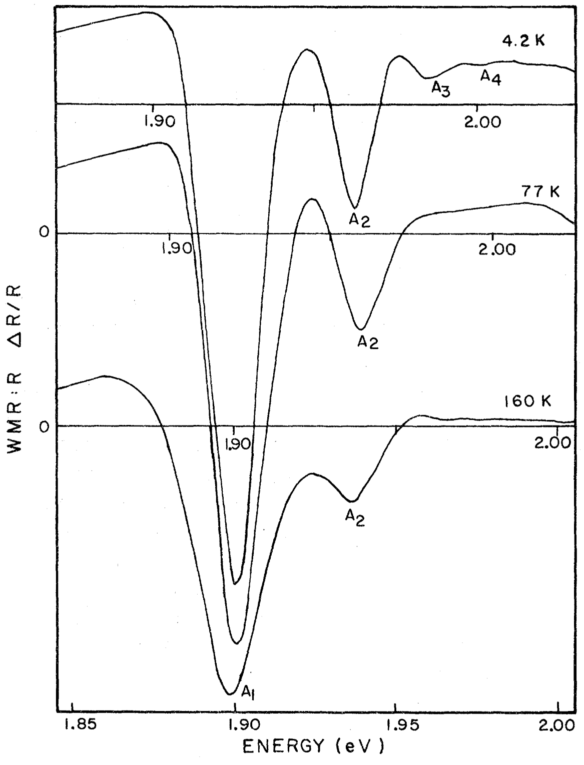

FIG. 2. Wavelength-modulated reflectivity spectra at different temperatures showing the evolution of the A peaks. Note the shifts in the energy axis.

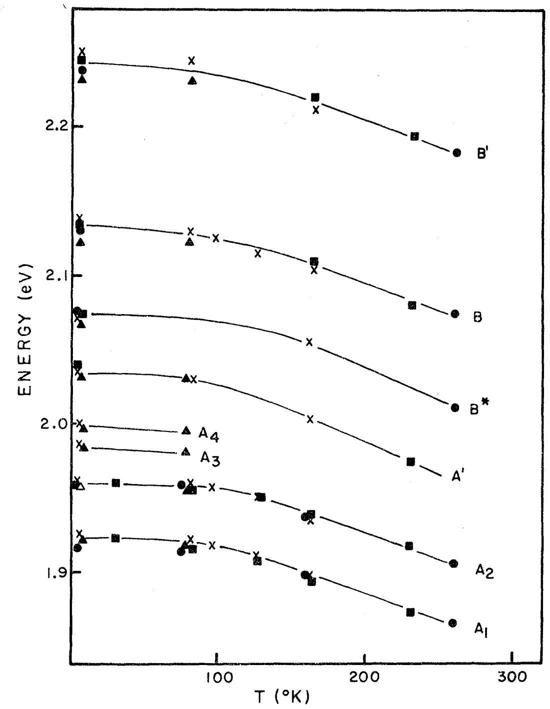

FIG. 3. Position of the spectral structures as functions of the temperature: ■, sample 1 (natural), WMR; ×, sample 2 (natural), WMR; ●, sample 3 (synthetic), WMR; ▲, samples 4, 5, 6 (natural), PC and PV.

The temperature broadening of some relevant structures is shown in Fig. 4. ΔE is the difference in photon energy between the two zero-points of each structure in the WMR spectrum, after correction for the contribution of adjacent structures. According to the general considerations of Sec. III A concerning the optical constant of MoS_2 in the excitonic region, this quantity corresponds to the half-width in the ϵ_2 spectrum. The temperature broadening shown in Fig. 4 corresponds to the theoretical behavior predicted by Toyozawa[27] for excitonic transitions. A very large natural broadening nearly independent of temperature below 100 K characterizes all the peaks; the value of θ_0 (105 K), deduced from Fig. 4, is much higher than in most semiconductors (20 to 50 K) and approaches values found in alkali halides (~150 K). In the Toyozawa theory[27] θ_0 can be directly related to the exciton reduced mass; the high value of θ_0 in MoS_2 thus indicates a high value of the exciton reduced mass. It may be mentioned that a high electron-effective mass was derived by Fivaz and Mooser[28] from the transport properties of MoS_2.

The disappearance of peak A_3 at 160 K and shoulder A_4 at 80 K suggests that these structures are members of the excitonic series, but at the same

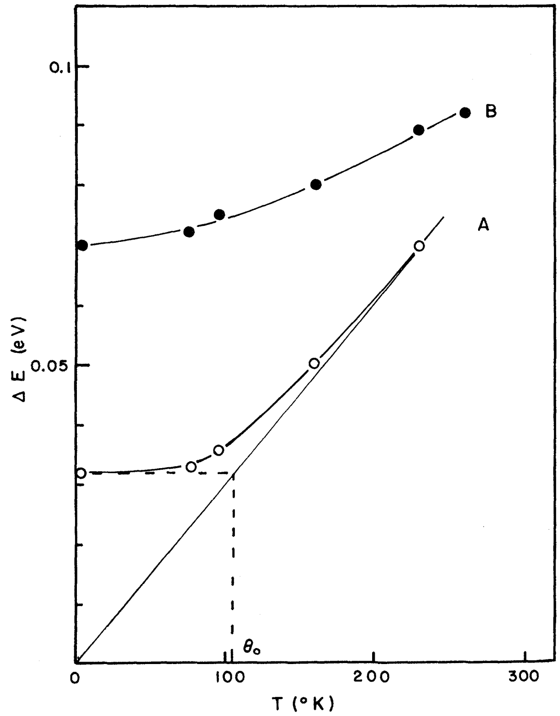

FIG. 4. Half-width of the A_1 and B structures as functions of the temperature.

time the structure A' observed at higher energy up to room temperature is not related to the same series. Also while A_2 tends to disappear at higher temperatures, B' seems more stable; the other important structure, B, does not appear to have any companion. We are thus led to recognize in the present spectra of MoS_2 one excitonic series constituted by the peaks A_1, A_2, A_3 and perhaps the shoulder A_4, and possibly the ground states of three other separate series in the peaks B, B', and A'. The low intensity and large width of B, B', and A' prevent the observation of the associated higher levels. Four independent transitions (B, B', A', and the series A) thus appear to characterize the direct-gap region in MoS_2; this is consistent with all band-structure calculations that show multiple conduction and valence bands in this energy range; it is also consistent with the spectra of the other Mo dichalcogenides all showing four transitions[28] in the band-gap region. The very low A-A' and B-B' separations, of the order of 0.1 eV, compared with the homologous separations of 0.4 eV in $MoSe_2$ and 0.65 eV in $MoTe_2$, as well as the very low intensity of A' and B' in MoS_2, are not immediately explainable; they could be related to the lower anion orbital overlapping and to the lower "*p*" content of the conduction band in MoS_2 as compared to the other Mo dichalcogenides.

C. Excitonic series *A*

The spectral positions and the relative intensities at 4.2 K of the structures in the excitonic series *A* are reported in Table II. The relative intensities do not follow the theoretical ratio $1/n^3$ that characterizes a first-class Mott-Wannier excitonic series and the spectral position of the peaks do not follow a hydrogenlike law (from the comparison with the theoretical positions obtained by assuming as correct the positions of A_2 and A_3) described by the relation

$$E_n = E_g - \frac{1}{n^2} R_e , \tag{2}$$

with $E_g = 2.0048$ eV and $R_e = 0.169$ eV. The weak shoulder A_4 corresponds with sufficient precision to the $n = 4$ level of the series, while a positive "ground" state shift $\Delta E = 90$ meV is found for A_1. The excitonic radii, deduced from the effective-mass approximation (EMA), are also reported in Table II. Because of the anisotropy of MoS_2, a dielectric constant[15] $\epsilon_0 = (\epsilon_\perp \epsilon_\parallel)^{1/2} = 4.3$ was used for the calculation.

Ground-state anomalies are very common in exciton spectra; the negative anomalies of the first line of the yellow and of the green series in Cu_2O are well known[29] as well as that exhibited by some excitons in solid rare gases.[30] Large positive anomalies were observed in PbI_2,[31] and more recently in alkali halides.[32] Indeed the effective-mass approximation which predicts a Rydberg series for excitons holds with sufficient precision only for a restricted number of semiconductors; however, a more correct pseudopotential theory developed by Hermanson and Phillips[33] (HP) shows that if some suitable microscopic corrections (the so-called "central cell corrections") are included, the EMA theory works well for both exciton and impurity states.

Three corrections to the hydrogenic theory were considered in the HP theory: (i) breakdown of macroscopic dielectric screening (BD) in the central cell, or spatial dispersion; (ii) large-*k* variation of the effective mass due to nonparabolic energy bands (*kE*); (iii) repulsive term (*R*) in the central cell arising from orthogonality requirements between the electron wave function and core orbitals. According to the general HP treatment, there is a substantial cancellation in the central cell between these three corrections only when "M_0" excitons in Γ_1 bands are involved; in that case, a nearly hydrogenic behavior of the excitonic series results; otherwise a positive or negative central cell correction may arise and direct calculations are needed for its evaluation. A detailed computation was carried out by Hermanson[34] for excitons and im-

TABLE II. Summary of experimental and EMA predicted values (with $R_e = 0.169$ eV) for the A excitonic series in MoS_2.

	Position (eV)		Intensity (referred to A_1)		Excitonic radius (Å)
	Experimental	EMA prediction	Experimental	EMA prediction	(EMA prediction)
A_1	1.9255	1.8356	1	1	9.7
A_2	1.9625	1.9625	$\frac{1}{15}$	$\frac{1}{8}$	39.5
A_3	1.986	1.986	$\frac{1}{100}$	$\frac{1}{27}$	89
A_4	1.999	1.994	⋯	$\frac{1}{64}$	158
A_∞	⋯	2.0048	⋯		⋯

purity states in rare-gas solids (minimum of the conduction band at Γ_1); the results, in good agreement with experiment, show a nearly complete cancellation between the negative contribution of the BD and kE terms and the positive R term. We shall give here an estimate of the different corrections for MoS_2 on the grounds of the HP theory.

The BD correction arises from the dependence of the effective-exciton dielectric constant on the exciton radius; for small r, this dielectric constant tends to unity while for $r \to \infty$ it becomes the static dielectric constant ϵ_0. The BD correction thus results in a negative exciton shift because of an attractive contribution to the electron-hole interaction; it cannot therefore explain the large positive "ground"-state shift in MoS_2. The correction would be at any rate negligible for MoS_2 because the ground-state exciton radius (~10 Å) is much larger than the dielectric-constant breakdown length (~1 Å), evaluated on the basis of the Penn[35] "semiconductor" model for the dielectric constant.

The correct evaluation of the kE term implies a complete knowledge of the conduction- and valence-band wave functions; according to Hermanson,[34] a rough estimate of the correction due to this term may be given, however, by considering the interpolation formula

$$\frac{m_0}{m^*(r)} = \frac{m_0}{m_0^*} - \left(\frac{m_0}{m_0^*} - 1\right) e^{-r/a}, \tag{3}$$

where a is of the order of the lattice parameter. For small r, $m^*(r)$ tends to the free-electron value m_0, whereas for $r \to \infty$ it tends to the zero-k effective mass m_0^*; the same relation may be assumed for the exciton reduced mass. The high value of the excitonic radius here makes this correction negligible (of the order of 10^{-3} eV on the EMA prediction).

Another possible cause of perturbation of the Wannier series is the anisotropy of the effective mass and of the dielectric constant. An EMA computation of the exciton states as a function of the anisotropy parameter $\gamma = \epsilon_\perp \mu_\perp^* / \epsilon_\parallel \mu_\parallel^*$ has been carried out independently by Faulkner[36] and by Baldereschi and Diaz[37]; the resulting correction to the hydrogenic series is positive and is larger for small γ. The value of $\mu_\perp^* / \mu_\parallel^*$ is not directly known for MoS_2 but it may be evaluated from the ratio of the conduction-electron magnetic susceptibilities in directions normal and parallel to the c axis, available from the experimental data of Dutta[38]; one finds $m_{e\perp}^* / m_{e\parallel}^* = 0.2$, a value that agrees well with those of other layered semiconductors, such as GaSe.[39] According to Evans and Young[15] $\epsilon_\perp / \epsilon_\parallel = 2.3$; we thus have, by assuming $\mu_\perp^* / \mu_\parallel^* = m_\perp^* / m_\parallel^*$, $\gamma = 0.46$. The above value of γ gives a correction of less than 1% to the ground-state energy. A complete correction could in fact be obtained only with an unlikely value of $\mu_\perp / \mu_\parallel$ as low as 0.004.

A strong positive central-cell correction may arise from the R term. The HP treatment of this contribution refers to the case of an impurity center; the orthogonality requirement between the electron wave function and the core orbitals introduces a repulsive central potential that reduces the electron-impurity binding energy. The repulsive potential represents in effect a polarization response of the core levels to the additional charge and gives rise to an "excluded volume" around the local center.

This correction works well also when applied to excitons with local character, such as in rare-gas solids[34]; for alkali halides a similar correction, also based on a repulsive potential but justified by the localization requirement of electrons in the anion and of holes in the cation sublattices, respectively, was recently proposed by Antoci and Nardelli.[40] As shown by Harbeke and Tosatti[41] (HT), the same repulsive potential also plays a fundamental role in the shallow excitons of PbI_2 and it gives a positive correction sufficient to explain the large "ground"-state shift found in this material. The reason for the applicability of a correction typical of a local center to nonlocalized excitons lies in the so-called "cationic" nature of excitons in PbI_2: that is, both valence and conduction bands arise from Pb orbitals; this leads to a very stringent electron-hole orthogonality requirement with a consequently short-range repulsive potential and "excluded volume" effect. The same mechanism may explain the analogous shift observed in MoS_2.

According to both the Mattheis[8] and Kasowski[9] band structures, the valence band of MoS_2 had a d_{z^2} character and the conduction band a $d_{x^2-y^2}$ or a d_{xy} character; both bands are thus mainly formed with Mo orbitals. This means that in MoS_2 as in PbI_2 we may speak of "cationic" excitons and that the use of the repulsive correction is well justified. According to HT, a lowest-order evaluation of the shift of a hydrogenic s state for this correction is given by

$$E(n)=\langle n|V_R|n\rangle=4R_e\frac{r_0^*}{a_{(1)}}\frac{1}{n^3}, \tag{4}$$

where r_0^* is the radius of the "excluded volume" and the other symbols have their usual meanings. A correct computation of r_0^* requires the knowledge of both valence- and conduction-band wave functions; however, a sufficient evaluation may be carried out by assuming that because of the cationic nature of the exciton, r_0^* corresponds, in practice, to the radius of the molybdenum cation. The screening effects of the solid modifies the dimension of the external orbitals so that it is more correct to take for r_0^* the mean radius of the elementary cell of the cationic sublattice, or in the present case $r_0^*=2$ Å. The application of (4) shifts all excitonic states of the A series, so that new parameters for the series must be derived.

Excitonic levels are now described by the relation

$$E_g-E(n)=\frac{R_e}{n^2}-4R_e\frac{r_0^*}{a_{(1)}}\frac{1}{n^3}. \tag{5}$$

Three excitonic transitions are sufficient to derive new values for E_g, R_e, and $r_0^*/a_{(1)}$; a useful check may be supplied by a fourth level. By using the three first A levels the following values are obtained for the series parameters:

$E_g=2.0127$ eV,

$R_e=0.3115$ eV,

$r_0^*/a_{(1)}=0.18$.

In Table III the two contributions to the binding energy of the different exciton states, derived with the above values, are shown separately; for the A_4 state the difference with respect to the experimental value, of the order of 2 meV, is comparable to the experimental error. The data of Table III show clearly that the repulsive central-cell correction is prevalent for the A_1 state and gives a minor relative contribution for the other states.

TABLE III. Experimental and calculated values of $E_G-E(n)$ (eV), with $E_G=2.0127$ eV and $R_e=0.3115$ eV.

	EMA	Theory R corrections [Eq. (4)]	Resultant values [Eq. (5)]	Experimental values
A_1	0.3115	−0.2243	0.0872	0.0872
A_2	0.0782	−0.0280	0.0502	0.0502
A_3	0.0347	−0.0080	0.0267	0.0267
A_4	0.0195	−0.0035	0.0160	0.0137

The excitonic radius $a_{(1)}$ of the A_1 state derived from $r_0^*/a_{(1)}$ gives a value of 11.1 Å, of the order of that predicted by EMA. The radii of the higher states may be evaluated with the EMA since the R correction is small for these states. The values of $a_{(2)}=21.5$ Å, $a_{(3)}=48$ Å, and $a_{(4)}=86$ Å thus calculated may be contrasted with the values of Table II.

The high value of R_e implies a high exciton reduced mass; it is $\mu^*=0.42m_0$, i.e., $m_{e\perp}^*\simeq m_{h\perp}^*\simeq m_0$, consistent with our results on exciton linewidth and with the Kasowski and Mattheis band structures that show very flat conduction and valence bands.

D. Magnetic field effect

The high effective mass found for excitons in MoS_2 should correspond to a high spectral stability against magnetic field. However, a shift of some structures in the excitonic spectral region was found at 77 K in magnetic fields of up to 25 kG by Evans and Young.[15] We sought a similar shift at 4.2 K in WMR and PC spectra with magnetic fields up to 70 kG for several samples, natural and synthetic, in both the Faraday and Voigt configurations; we were not able to detect any spectral change larger than the signal fluctuation. If both the effects of the linewidth and the noise are taken into account, it may be assured, in effect, that for any of the observed structures the eventual shift did not exceed 2 Å ($\Delta E\simeq 6\times10^{-4}$ eV) even at the highest magnetic fields.

From the band structure, as well as from the values of the electron and hole mobilities, it appears likely that electron and hole effective masses in MoS_2 are comparable; therefore the shift of excitonic structures in magnetic fields should arise mainly from the diamagnetic term: it should be proportional to B^2 and to n^4. Replacing ϵ^2 in the Schiff and Snyder[42] formula by $\epsilon_\perp\epsilon_\parallel$, the limitation $\Delta E(3)<6\times10^{-4}$ eV at 70 kG for the A_3 excitonic level may be calculated to imply for the reduced mass the limitation $\mu^* \gtrsim 0.3m_0$, in good agreement with the value obtained from the analysis of the series.

IV. CONCLUSIONS

A first result obtained from the analysis of the PC and WMR spectra of MoS_2 has been the evidence of four independent transitions in the spectral region 2–2.2 eV, i.e., the peaks A', B, B' and the excitonic series A; this rules out an apparent anomaly for MoS_2 that was hitherto thought to show only two transitions (A and B), in disagreement with the band structure[8,9] predictions and in contrast to observations in other Mo dichalcogenides. A second result has been the identification of the members of the excitonic series A and the deduction of its parameters.

The more relevant features of this exciton, i.e., its large ionization energy and the high value of its reduced mass, are well supported by (i) the study of the series and its fitting to a theoretical model; (ii) the lack of any structure shift larger than 2 Å with magnetic fields up to 70 kG; (iii) the large linewidth of the excitonic structures; (iv) the high stability against temperature of the peak A_1. Some previous evidence also gives support to the above results: (i) the Fivaz and Mooser[28] study on the temperature dependence of the transport properties of MoS_2; (ii) the band-structure calculations that show very flat valence and conduction bands.

The large "ground"-state anomaly of the excitonic series has been explained with a repulsive central-cell correction according to the HP theory; its applicability to MoS_2 has supplied a proof for the cationic nature of excitons and consequently a good support to the Kasowski and Mattheis band structures that predicted d-like conduction and valence bands, both originating from Mo orbitals, and a 2-eV direct gap fully corresponding to experimental evidence.

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