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Fundamental absorption edges and indirect band gaps in $W_{1-x}Mo_xSe_2$ ($0 \le x \le 1$)

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Abstract. The optical absorption edge $(E \perp c)$ was measured on basal-plane samples of single-crystal $W_{1-x}Mo_xSe_2$ ($0 \le x \le 1$) at temperatures of 15, 78 and 295 K. The data were fitted to several expressions for the shape of the edge, with the best fit being to that expected for indirect allowed transitions. The phonon involved is in an optical branch, and its energy varies smoothly with x. The band-gap energy at any temperature varies smoothly with x, indicating that the band edges are the same for MoSe₂, WSe₂ and the compounds of intermediate compositions.

1. Introduction

 $MoSe_2$ and WSe_2 are members of a class of layered semiconducting transition-metal chalcogenides, which includes other chalcogenides of these two transition metals (Wilson and Joffe 1969, Kalikhman and Umanskii 1972). The transition metals are surrounded by six chalcogens in a trigonal prism. These prisms form sheets with upper and lower surfaces containing only hexagonally disposed chalcogen atoms with saturated bonds, sheets that are van der Waals bonded into the three-dimensional crystal. Early discussions of these materials pointed out that the upper part of the valence band should be based on non-bonding d orbitals of the transition metals, and the conduction band minimum on non-bonding chalcogen orbitals. This led to the idea that these compounds would make good materials for electrodes for liquid-junction photovoltaic cells, as the instability of the photoexcited state should be less than in other materials, e.g. GaAs, in which the photohole is in a bonding band (Tributsch 1977). Such proved to be the case and rather efficient, long-lived photovoltaic cells have indeed been produced (Kautek et al 1980, Kline et al 1982, Kam and Parkinson 1982). The band gaps of many of these materials are around 1 eV, and it has been suggested that the band gaps are indirect. Evidence for this is not abundant. The most elaborate band calculation, that of Matheiss (1973) for MoS₂ (and other transition-metal chalcogenides of different natures), indicates that the conduction band minimum is along the symmetry line T in

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§ Operated for the US Department of Energy by Iowa State University under contract No W-7405-Eng-82. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences. the Brillouin zone, while the valence band maxima are either at the zone centre, Γ , or the centre of a zone edge, K. In either case, the band gap is expected to be indirect. In fact, the calculations show that the valence band maximum at Γ is highest, but there are two different maxima at K within 0.3 eV of the maximum at Γ . The accuracy of such a calculation does not allow one to identify the true maximum with confidence. This calculation was not carried out on materials with heavier elements because a relativistic treatment would have been required. (See also Doran (1980).) Some experiments to elucidate the nature of the valence band maxima were carried out by Fonville *et al* (1970).

There is some experimental evidence for the indirect nature of the gap in some of these materials. Goldburg et al (1975) measured the absorption edge of MoS_2 and $MoSe_2$. They fit the energy dependence of the absorption edge to that expected for direct and indirect transitions, finding a better fit for the indirect process. There is good evidence that the edge is indirect in MoS_2 , $MoSe_2$ and WSe_2 from the spectral dependence of the photoyield of electrochemical cells (Kautek et al 1980, Kam and Parkinson 1982). These studies provided convincing evidence of the indirect gap expected from the band calculation, and gave values for the gap, but the involvement of phonons has not been demonstrated quantitatively. There have been several optical studies made of these compounds, including modulation spectroscopic studies, but all of these to date deal with the absorption above the edge (Amirtharai et al 1982, Beal et al 1972, Beal and Liang 1976, Fortin and Raga 1975, Ito et al 1981, Liang 1973, Meinhold and Weiser 1976, Saiki et al 1978). They begin at the energy of the direct band gap and its accompanying exciton, labelled A, and continue to higher energy. These studies are reviewed by Evans (1976). The work reported below is at lower energies, and deals with the indirect gap below the direct gap.

In the following we report measurements of the absorption edge of single crystals of $MoSe_2$ and WSe_2 , and of several mixed crystals $W_{1-x}Mo_xSe_2$ (Brixner and Teufer 1963). These were carried out at several temperatures and analysis of the data leads to the following conclusions. Both $MoSe_2$ and WSe_2 have indirect band gaps. The energy of the gap has been determined at three temperatures and the energy of the optical phonon involved in the absorption was determined. Measurements on the mixed crystals show that these, too, have indirect gaps, with an optical phonon involved for momentum conservation upon photon absorption. This shows that there is little scattering from the cation disorder: k is still a reasonably good quantum number. The smooth variation of the energy gap with composition indicates that the nature, i.e. symmetries, of the band edges in $MoSe_2$ and WSe_2 is the same, whatever it may be.

2. Experimental details

 $W_{1-x}Mo_xSe_2$ was synthesised, then grown into single crystals by chemical vapour transport. Powders of W (99.98%), and/or Mo (99.9+%) were weighed and mixed with weighted Se shot (99.999%), then sealed in a cleaned quartz ampoule. This was evacuated to about 10^{-5} Torr, slowly heated to 950 °C in a horizontal furnace, and maintained there for a week, yielding a dark powder. This powder was transferred to another quartz ampoule and freshly etched in 48% HF in the hope of producing nucleation sites. After evacuation to about 10^{-5} Torr, chlorine gas at about 400 Torr was introduced and the ampoule sealed. The ampoule was placed in a horizontal three-zone furnace (hot zone at about 975 °C, cold zone at 940 °C with about 1 °C cm⁻¹ gradient). Transport was

carried out for two to three weeks. Growing mixed crystals was considerably more difficult than growing pure compounds.

The resultant crystals were thin plates with thicknesses from ten to several hundred μm , and surface areas up to about 1 cm. Thicknesses over 100 μm were measured with a micrometer or optical microscope, while a scanning electron microscope was used for thicknesses under 100 μm . Because of the geometry of the growth ampoule and contact from neighbouring crystals, most of the crystals had macroscopic defects. X-ray powder patterns showed that the pure crystals, MoSe₂ and WSe₂, were of the 2H polytype. X-ray microprobe analysis gave the Mo/W ratio for the mixed crystals. It was always close to that based on the weights of the starting materials.

Samples were prepared by cleaving with Scotch tape. They were either used ascleaved, or immersed in 2M HCl for about 30 s, rinsed in triply distilled water, then rinsed in trichloroethane, acetone and alcohol. They were mounted over apertures in phosphor-bronze sheets which were then placed in a cryostat. To avoid thermally induced strains, the samples were held to the bronze by a small dot of General Electric 7031 varnish. The optical measurements were made on a Cary 14R spectrophotometer using apertures in the reference beam that were nearly identical to those under the sample. Temperatures of 295 K, 78 K and about 12–15 K were achieved with liquid nitrogen and liquid helium. The samples were not immersed in the liquid helium, so their temperatures were as quoted above. The uncertainty in this temperature is not important, as will be explained below.

3. Results

The transmission of the thin crystal samples was measured at normal incidence with the electric vector of the measuring light perpendicular to the *c* axis of the crystal. Thus only one component of the absorption coefficient is reported. The absorption coefficient, α , for a sample of thickness *d* was obtained from the transmission, I/I_0 , from

$$I/I_0 = (1-R)^2 e^{-\alpha d} / [1-R^2 \exp(-2\alpha d)].$$
(1)

This assumes there are multiple reflections within the sample, but that they add incoherently due to sample inhomogeneity or a sufficiently large spread of angles of incidence. They are negligible, coherent or incoherent, when αd becomes *large*. R is the reflectance of a semi-infinite sample; for regions of low absorption, such as occur here, it can be obtained from the refractive index, n, as via

$$R = (n-1)^2/(n+1)^2.$$
 (2)

Three methods were used to find R, which, in principle, depends on photon energy, thus varying within our range of measurements. One was to use literature values for the pure compounds. The second was to make use of thin samples and equation (1), which reduces to

$$I/I_0 = (1 - R)/(1 + R)$$
(3)

where αd is small. Thus R came from transmission measurements far below the absorption edge. In this range interference fringes were seen frequently, as were small oscillations in I/I_0 . These result from coherent addition of multiple beams in the sample. Equation (1) is then valid only for a transmission averaged through the fringes. The fringe spacing, however, gives n if d is known, and R can be found from n. All three of

these gave results agreeing to within a few per cent for WSe_2 , for which most such data were taken. The 295 K *R*-spectrum for WSe_2 was used for this material and all the other compounds studied at all temperatures. This will introduce some error, but this is reduced by our further treatment of the data.

Figure 1 shows that absorption coefficient of WSe₂ at the absorption edge at 295, 78 and 15 K. There is a structureless rise as energy increases, with some change in shape. Around 1.32 eV there is a hint of underlying structure in the data for 15 K. The absorption coefficient at lower energies is constant and not shown. There are several possible origins of the constant absorption at lower energies. One is that the apertures in the two beams may not be identical. We believe this has been balanced out adequately at 295 K, but possibly inadequately at lower temperatures because of the motion of the cooled aperture in the cryostat. (The flux in the two beams in the spectrophotometer is not homogeneous, so motion of an aperture can change the detected flux.) Another is that the value of R may be erroneous, which would then simulate a constant absorption coefficient. The third is that there may be true absorption in this region. Free-carrier absorption can be appreciable here, for the carrier concentrations were of the order of



Figure 1. Absorption coefficient, α (plotted as $(\alpha h\nu)^{1/2}$ against energy $(h\nu)$) for a single crystal of WSe₂ ($E \perp c$) at (A) 295, (B) 78 and (C) 15 K. The circles are the measured values. The full curves are the fit to (1) with l = 2 and the parameters listed in table 2. (A constant has been subtracted from α ; see the text.)



Figure 2. Absorption coefficient, α (plotted as $(\alpha h\nu)^{1/2}$ against energy) for several mixed crystals of W_{1-x}Mo_xSe₂ at room temperature (295 K). The points are the measured values. The full curves are the fit to (1) with l = 2 and the parameters listed in table 2. (A constant has been subtracted from α ; see the text.) The values given on the curves are of x.

 10^{17} cm⁻³ for WSe₂ as determined by transport measurements on some of our samples (Kam 1982). (They were not known for the other samples.) Free-carrier absorption should increase with decreasing photon energy and it should decrease at lower temperatures if phonon scattering is important. There can also be absorption from impurities deep in the gap. This could give the structure around 1.32 eV in figure 1. Such structure could be masked at higher temperatures by the edge that moves over it, or it could disappear as the initial states ionise thermally.

Figure 2 shows the absorption-edge spectra for the $W_{1-x}Mo_xSe_2$ samples, including those for MoSe₂, all measured at 295 K. Data were obtained for each of these samples at 78 and 15 K as well, but these are not displayed.

Different shapes are expected for the absorption edge for different types of band edges. We neglect excitonic effects for now. Direct interband transitions may be allowed or forbidden by the symmetries of the band-edge wavefunctions. Phonons are not needed to conserve momentum, but phonon absorption and emission broadens the edge. The spectral dependence of the edge will be as $(E - E_0)^p$ where E is the photon energy and E_0 is the band-gap energy, a function of temperature. The exponent p depends on the dimensionality of the bands and on whether the transitions are allowed or forbidden. Indirect transitions require a phonon (in pure semiconductors) for momentum conservation. The absorption edge then is expected to vary as

$$\alpha = \begin{cases} 0 & h\nu < E_0 - k\theta \\ \frac{A}{h\nu} \frac{(h\nu - E_0 + k\theta)^p}{(e^{\theta/T} - 1)} & E_0 - k\theta \leq h\nu \leq E_0 + k\theta \end{cases}$$
(1)
$$\frac{A}{h\nu} \left(\frac{(h\nu - E_0 + k\theta)^p}{(e^{\theta/T} - 1)} + \frac{(h\nu - E_0 - k\theta)^p}{(1 - e^{-\theta/T})} \right) & h\nu > E_0 + k\theta \end{cases}$$

with $k\theta$ the energy of the phonon involved in momentum conservation (Ridley 1982). The foregoing assumes only one phonon branch is predominant, and that phonon scattering of just electrons or of just holes is predominant. Again the exponent p depends on the dimensionality of the bands and on whether the transition is symmetry-allowed or not. Possible values of p are given in table 1 (Lee et al 1969). The data were fitted to an expression of this form for each possible value of p. A least-squares fit was made to the room-temperature data for each sample, using a fixed p and treating E_0 , A, $k\theta$ (where required) and a constant background absorption, B, as parameters. A meansquare deviation was obtained, as well as a plot of calculated values to see if deviations were systematic. At this point it was already clear that p = 2 allowed indirect transitions in a three-dimensional crystal, or forbidden indirect transitions in a two-dimensional crystal, gave a better fit. The low-temperature data were then fitted, first allowing A, B, E_0 and $k\theta$ to be minimisation parameters. This produced fits with some scatter, a few meV, in k θ . Since the temperature dependence of the phonon energy is expected to be very small on a meV scale, the data were refitted by keeping $k\theta$ at its room-temperature value. The justification for this, and the reason for the scatter, is that at room temperature both the terms for phonon absorption and phonon emission contribute to the spectrum, but at low temperature the phonon absorption term is very small and contributes little to the spectrum, its contribution being partly subsumed in the constant term B. This being so, errors in the temperature, which may be a few K at 15 K, play little role, for with fixed $k\theta$ and only a phonon absorption term the error in T is taken up as an altered value of A. (A may, in fact have a slight intrinsic temperature dependence.) The procedure of fitting with A, B, E_0 and $k\theta$ at 295 K, but keeping $k\theta$ fixed at lower temperatures was followed in all the data analysis. The fits for allowed indirect transitions are given in figures 1 and 2 as the full curves. The resultant parameters are given in table 2.

It is difficult to assess the accuracy of the parameters derived from the foregoing. Forcing $k\theta$ to change by 1 meV produced plots that were equally close to the data when plotted, but for which the average squared deviation approximately doubled. Thus an error of about $\pm 1 \text{ meV}$ might be assigned to $k\theta$ and E_0 ; changing by several meV produced poorer fits. However, different values of E_0 and $k\theta$ could be obtained by fitting a different energy range, i.e. by rejecting some points at lower or higher photon

Type of	D	irect	Indirect		
transition	two-dimensional	three-dimensional	two-dimensional	three-dimensional	
Allowed	0 (step function)	1/2	1	2	
Forbidden	1	32	2	3	

Table 1. Values of the exponent p for different types of band-gap transitions.

Table 2. Absorption-edge	fitting parameters	$W_{1-x}Mo_xSe_2$.
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x	Temperature (K)	E_0 (eV)	<i>kθ</i> (eV)	$A (cm^{-1} eV^{-1})$	B (cm ⁻¹)
0	295 78 15	$\left.\begin{array}{c}1.219\\1.261\\1.265\end{array}\right\}$	0.029	2643	$ \begin{cases} 5.1 \\ 6.0 \\ 5.5 \end{cases} $
0.2	295 78 15	$\left.\begin{array}{c}1.185\\1.218\\1.223\end{array}\right\}$	0.026	2322	$\begin{cases} 25.5 \\ 25.9 \\ 25.9 \end{cases}$
0.5	295 78 15	$\left. \begin{array}{c} 1.163 \\ 1.195 \\ 1.198 \end{array} \right\}$	0.024	3401	$\begin{cases} 18.1 \\ 18.4 \\ 18.5 \end{cases}$
0.75	295 78 15	1.136 1.170 1.177	0.025	2192	$ \begin{cases} 37.6 \\ 39.5 \\ 38.3 \end{cases} $
1	295 78 15	$\left. \begin{array}{c} 1.122 \\ 1.162 \\ 1.164 \end{array} \right\}$	0.025	2326	$\begin{cases} 26.1 \\ 26.4 \\ 25.9 \end{cases}$

+ The last figure is uncertain by ± 2 to ± 4 .

energies. We avoided using data at higher energies than those shown (from thinner crystals) because of the possibility of new interband transitions. The band calculations show two nearly degenerate but inequivalent valence band maxima which could give rise to two overlapping edge structures. Limiting the data range reduced the probability of including such transitions. It also made little sense to go to energies much below

Fable 3. Indirect band	l gaps	(eV)) at 295	Κ.
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	WSe ₂	MoSe ₂
This work	1.219	1.122
Kam and Parkinson (1982) (photoyield)	1.20	1.09
Kautek et al (1980) (photovield)	1.16	1.06
Goldburg <i>et al</i> (1975) (optical absorption)	_	1.09
Grant <i>et al</i> (1975) (transport)	-	1.6
Agarwal <i>et al</i> (1983) (transport)	0.51	0.38

 $E_0 - k\theta$ because it is not clear that the constant B is adequate, due to the expected energy dependence of R and of free-carrier absorption. Fitting data on different samples gave parameters quite close to those in the table, even though there were differences in the absorption spectrum (shifts in energy) due to errors in sample thickness.

The band gaps for $MoSe_2$ and WSe_2 at 295 K do not agree well with the gaps determined from electrical measurements (Grant *et al* 1975, Agarwal *et al* 1983). The gaps for both WSe_2 and $MoSe_2$ at 295 K are in better agreement with those determined from photoyield spectra (Kautek *et al* 1980, Kam and Parkinson 1982). (See table 3).

4. Discussion

It is clear that the expression for indirect symmetry-allowed interband transitions gives a good account over a wide temperature range of the absorption edge in WSe₂, MoSe₂ and mixed crystals. (Indirect, symmetry-forbidden transitions in a two-dimensional crystal fit equally well but despite the high anisotropy, true two-dimensional behaviour seems unlikely. The choice between these two possibilities does not affect the following discussion.) The values of the phonon energies in table 2 show that these are phonons in one of the numerous optical branches, not acoustic phonons. Infrared and Raman scattering data give values for some of the optical-mode phonon energies at the centre of the Brillouin zone. These range fom 21 to 36 meV in MoSe₂ and from 22 to 30 meV in WSe2 (Lucovsky et al 1973, Mead and Irwin 1977, Uchida and Tanaka 1978, Wieting et al 1980). The TO-LO splitting is very small in these materials, less than 1 meV (Uchida and Tanaka 1978). These are zone-centre phonon energies. The optical branches are relatively flat as compared with acoustic branches, but since the phonon momentum needed for an indirect interband transition is large, agreement of the phonon energies in table 2 with zone-centre LO phonon energies is not expected. The increase in phonon energy as W substitutes for Mo is genuine. The larger mass would generally cause a decrease in phonon energy; however, not only may force constants change, but also the wavevector of the phonon needed to conserve momentum in the indirect absorption process may change if the position of the conduction band minimum in the Brillouin zone changes with composition.

Table 3 shows indirect band gaps obtained by earlier absorption measurements (Goldburg *et al* 1975) and by extrapolations of the photoyield edge (Kautek *et al* 1980, Kam and Parkinson 1982). Our values are somewhat higher, by more than the value of $k\theta$. (The expected threshold would be $E_0 - k\theta$.) We believe our values to be somewhat more accurate because we fit data at energies near the band-gap energy rather than extrapolated data taken well above the gap energy into the gap region.

The temperature dependence of the band gap is shown in figure 3, displaying typical shapes for semiconductors. Three points do not allow an accurate determination of the temperature dependence. Use of the 300 and 78 K points gives an estimate of the linear temperature coefficient expected at temperatures well above the Debye temperature. (This may be an underestimate, for 78 K may be low enough that the temperature dependence of the gap to be getting smaller.) This gives $dE/dT = -2.5 \times 10^{-4} \text{ eV}$ K⁻¹ for MoSe₂ and WSe₂. This coefficient is a bit smaller than that reported in an early study of the absorption edge of WSe₂ over the same temperature range, $-4.6 \times 10^{-4} \text{ eV}$ K⁻¹ (Upadhyayula *et al* 1968). The direct exciton (A) has a temperature coefficient of $-3.0 \times 10^{-4} \text{ eV}$ K⁻¹, essentially the same as that for the indirect edge (Antoci *et al* 1972, Anedda *et al* 1979).

Figure 2 shows that the absorption edge shifts smoothly with x and that the edge can be fitted by an indirect model with a phonon to conserve momentum. There is no evidence of disorder scattering as a momentum-conserving process. Figure 4 shows the dependence on x of the band gap at 300 and 15 K. The change in gap energy is smooth. There are no abrupt slope changes, indicating that a different valence band maximum might be replacing that for MoSe₂ as x increases. Thus we can conclude that the band



Figure 3. Optical indirect band gaps of $W_xMo_{1-x}Se_2$ against temperature. The curves are not fits, as there are only three points to fit, but just visual guides. The values on curves are of x.



Figure 4. Optical indirect band gap of $W_xMo_{1-x}Se_2$ against x for (A) 78 and (B) 295 K. The curves are least-squares fits to $E(x) = E(0) + bx + cx^2$, with the parameters given in table 4.

edges are the same in all of these compounds. There is no change in the nature of either the valence band maximum or the conduction band minimum. There is also no evidence for the occurrence of second valence band maxima within about 0.1 eV of the highestlying one. The maximum at K must lie at least 0.1 eV lower than the one at Γ , assuming the latter to be the higher. The disorder on the transition-metal lattice does not seem to provide enough scattering to either contribute to the indirect edge or mix the K and Γ valence band maxima.

For *direct* band gaps in mixed III-V semiconducting compounds, it is customary (see, e.g., Van Vechten and Bergstresser 1976) to express the composition-dependent gap energy as

$$E(x) = E(0) + bx + cx^2$$

with c called the bowing parameter. For our *indirect* gaps, if we fit E(x) to this expression, we get the results shown in table 4. The uncertainty in c, the bowing parameter, is about ± 0.024 eV, using the estimate of Hildebrand (1956).

We have neglected exciton effects on the indirect edge. Their inclusion does not lead to peaks, but to an altered shape for the edge. For allowed indirect transitions, the exponent p will change from 2 to $\frac{3}{2}$ in the region above the edge, and there will be weak structure at energies one exciton Rydberg, R_{ex} , below $E_0 - k\theta$ (Elliott 1957). Excitons created at the direct gap, the so-called A and B exciton series, have values of R_{ex} that are strongly dependent on the model used to analyse the absorption spectrum. An early value for WSe₂ is $R_{ex} = 0.055 \text{ eV}$ for the A exciton (Beal and Liang 1976), but a later study, which resolved more structure, used a different model to get $R_{ex} = 0.189 \text{ eV}$ (Anedda *et al* 1979). The larger value implies a much larger exciton reduced mass. The A exciton will have a hole of the same valence band maximum as any indirect exciton, but the electron will be in a different part of the conduction band. If an exciton Rydberg as large as 0.1 to 0.2 eV were valid for the indirect exciton, such a good fit of our data

Т (К)	Least-squares fit to $E(x) = E(0) + bx + cx$			
	$E_0 (eV)$	b (eV)	<i>c</i> (eV)	
78	1.258	-0.176	0.082	
295	1.216	-0.138	0.044	

Table 4. Band gap of $W_{1-x}Mo_xSe_2$ for various values of x.

with p = 2 would not be expected. The electron-hole interaction should influence our spectra over a range of several exciton Rydbergs, hence over our entire spectrum for such a large R_{ex} . We suspect that the indirect exciton has a value of R_{ex} well under 0.189 eV.

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