IOPscience

Absorption from the excited state in ZnS:Mn

Absorption from the excited state in ZnS : Mn

J Dreyhsig† and J W Allen

Wolfson Institute of Luminescence, Department of Physics and Astronomy,
University of St Andrews, St Andrews, Fife KY16 9SS, UK

Abstract. An argon-ion laser has been used to populate the $^4T_1(^4G)$ first excited state of manganese in ZnS. Optical absorption from this state to ones of higher energy has been identified by its phase relation with the manganese luminescence when the light is chopped. The induced absorption consists of four bands and a rising feature at higher energy. Attempts have been made, unsuccessfully, to fit the energy levels by crystal-field or covalency models. The rising feature is thought to be due to photo-ionisation from the $^4T_1(^4G)$ state to the conduction band.

1. Introduction

Manganese-doped zinc sulphide is of technological importance because of its use in electroluminescence displays. It is also of scientific interest, partly because the manganese has a half-filled d shell and partly because ZnS occupies an intermediate position between the semiconductors and the insulators. Consequently there have been many investigations of its properties: reviews of some of these have been given by Gumlich (1981) and by Goede and Heimbrodt (1988). Some major problems remain unsolved, for example the positions of the manganese energy levels relative to the conduction and valance bands.

The present paper concerns excitations within the d^5 configuration of manganese. Since the work of Kröger (1939) it has been known that the absorption spectrum of ZnS:Mn contains five bands. Their widths are ~0.15 eV and their oscillator strengths are small, ~10^{-6}. Zeeman and piezospectroscopic measurements on the zero-phonon lines of the first three bands show that they correspond to transitions from the $^6A_1(^6S)$ ground state of the d^5 configuration to the $^4T_1(^4G)$, $^4T_2(^4G)$ and $^4E(^4G)$ excited states. The assignments of the two higher bands are controversial. Luminescence, with a decay time about 1 ms, results from a transition from the lowest excitation state to the ground state, $^4T_1$–$^6A_1$. The long lifetime of $^4T_1(^4G)$ is a result of the radiation transition being forbidden by spin and symmetry, while the non-radiative rate is small because of the large energy interval, 2.1 eV. Excitation to the higher levels is followed by rapid non-radiative transitions to the $^4T_1(^4G)$ level and then a radiative transition to the ground level. There should be other excited levels at higher energy but in an absorption measurement they are masked by absorption across the ZnS energy gap with a threshold at room

† Present address: Technische Universität Berlin, Institut für Festkörperphysik, Sekr PN4-1, Hardenbergstrasse 36, D-1000 Berlin 12.

temperature of 3.7 eV. Kushida *et al* (1974) took advantage of the long lifetime of $^4T_1(^4G)$ to investigate these levels. They used laser radiation to create an appreciable population of $^4T_1(^4G)$ and used another light source to probe absorption from $^4T_1(^4G)$ to the higher levels. In the present paper we confirm and extend the results of Kushida and co-workers. Their paper will be referred to as KTO.

2. Experimental apparatus

Although weak zero-phonon lines can be seen at liquid-helium temperatures, the absorption and emission of ZnS:Mn is predominantly in bands whose width does not change greatly with temperature. Also, in good material there is no thermal quenching of the $^4T_1(^4G)$ excited-state lifetime at room temperature. For these reasons, and for experimental convenience, our measurements were made at room temperature. This also avoided the bulk darkening unconnected with manganese that can occur in illuminated ZnS at low temperature.

A single crystal of melt-grown ZnS:Mn from Eagle–Picher with nominal concentration 0.5% Mn was used. Its dimensions were $9 \times 7 \times 13$ mm^3. The absorption path length was along the 9 mm axis and was made to go through part of the crystal with good optical properties by means of an entrance aperture. The source of the probe light for the absorption measurements was a 55 W tungsten–halogen lamp, slightly under-run for stability, run from a stabilised power supply. Because of the high refractive index of ZnS the sample could cause deviation of the optical path so care was needed in alignment. After the probe light had passed through the sample it was dispersed by a Monospek 1000 monochromator equipped with suitable gratings and was detected either by a photomultiplier (EMI 9558B) or a PbS infrared cell (Mullard 62SV). Filters removed higher-order signals. The spectral range covered was 350 nm–2.7 µm (3.55–0.46 eV). A phase-sensitive detector (PSD) was connected to the optical detector output. In order to pump the manganese from the ground state to the excited state, or to induce other transitions, either a tungsten–halogen lamp or a laser was used. The tungsten–halogen lamp was 150 W rating but run at 85 W input. Light from it was passed through two heat filters (Ealing 26-3053). Colour filters and a shutter could be inserted in the beam. The laser was an Ar-ion Spectraphysics 170 operated at the 514.5 nm line with a power of 1 W. This wavelength falls between the maxima of the first two excitation bands of ZnS:Mn, thus giving excitation via the flanks of these bands. At the sample the beam diameter was 8 mm giving a power density of about 2 W cm^{-2}. A chopper could be inserted in the laser beam or in the probe beam before the sample: it provided the reference for the PSD. Because of the small size of the absorption changes in some parts of the spectrum it was necessary to make sure that mechanical vibrations from the chopper were not transmitted to the rest of the apparatus.

For most experiments the pump and probe beams were perpendicular. Their dimensions, e.g. the width of the probe beam with respect to the absorption depth of the pump beam, were chosen to optimise the interaction region as regards size and homogeneity. For one experiment it was necessary to measure the luminescence when both the pump and the probe beam acted together as excitation sources. The two beams, one from the laser and the other from a tungsten–halogen lamp, were then aligned along the sample to traverse the same path in opposite directions, while the luminescence was observed in a perpendicular direction by a photomultiplier preceded by a 580 nm filter with FWHM 10 nm. In this particular experiment, narrow pass filters centred on 400, 420, 440, 460,
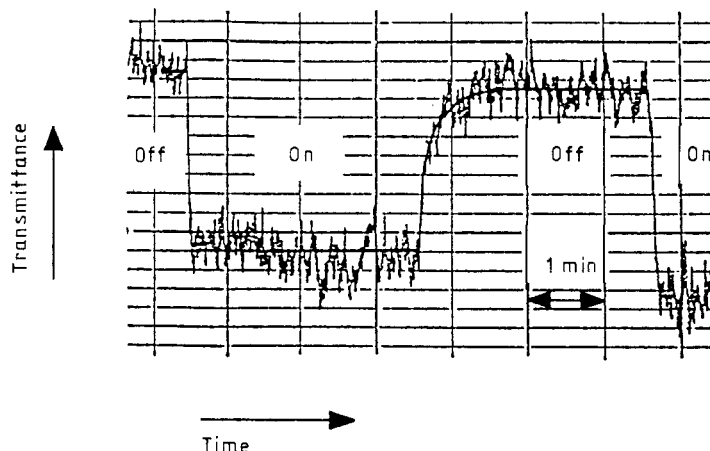
Figure 1. The time dependence of the absorption at about 625 mm (1.98 eV) induced by white light illumination.

480 or 500 nm, FWHM 10 nm, i.e. 3.10, 2.95, 2.82, 2.70, 2.58 or 2.48 eV could be put in the probe beam.

Measurement of optical power densities, when necessary, were made with a Hilger–Schwarz thermopile.

3. Experimental results

3.1. Absorption induced by a white pump light

It is known that when ZnS is illuminated at low temperatures a darkening of the crystal can occur, the induced absorption spreading throughout the visible region (e.g. Dieleman *et al* 1964). This absorption caused problems in the measurements of KTO so it was necessary to determine its effect on our room temperature measurements and to separate it from absorptions associated with manganese.

An initial measurement was made in which the scanned transmission spectrum was measured with the probe light being chopped without the pump light, then the pump light was shone onto the sample for five hours, then the transmission spectrum was measured again. No spectral change could be detected above the long-term drift of the measuring system.

To overcome the drift problem, the effect of a short pump light exposure was measured point by point in the wavelength. At each wavelength the pump light shutter was opened for three minutes then closed for a further three minutes before the next wavelength. The recorder trace of signal as a function of time showed a transient corresponding to increased absorption, with a fast rise time, a steady value during the three-minute pump illumination, and a decay time of about 0.5 min, as shown in figure 1. This pattern was repeated throughout the spectral range investigated, which was limited to the visible because of the low sensitivity of the PbS cell. A spectrum was obtained from the magnitude of the transient normalised to the direct transmission signal at each wavelength and is shown in figure 2. The error bars were estimated from reading errors in the amplitude of the transient since these were the dominant source of inaccuracy. The effect is small: at 550 nm (2.2 eV) the fractional change of transmission
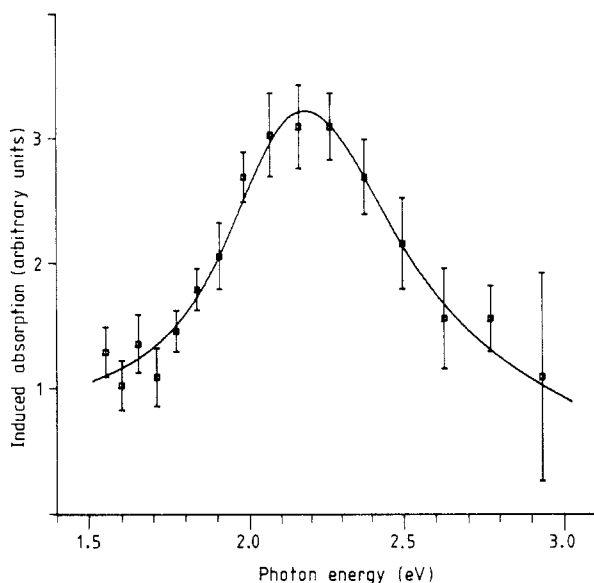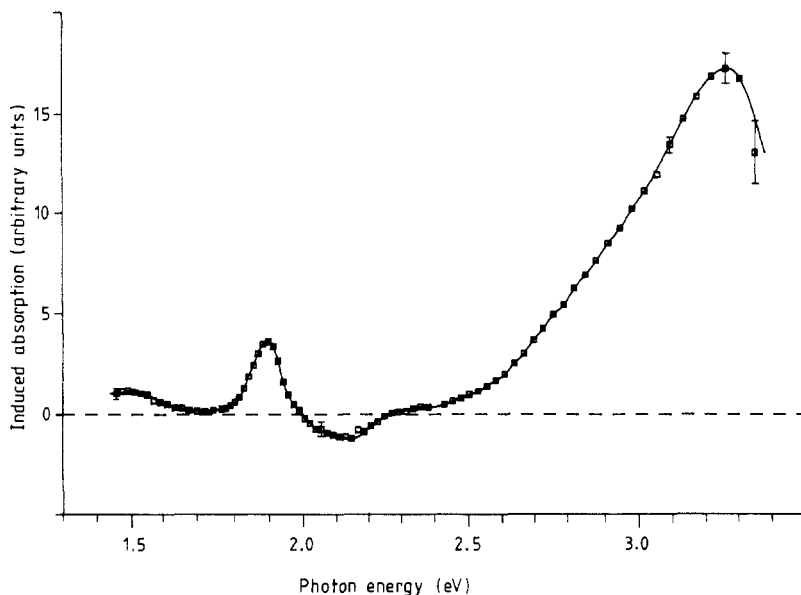
Figure 2. Spectrum of the absorption induced by white light illumination.

is about 0.5%. To get further information on the effect of different pump wavelengths on the induced absorption the measurement of induced absorption at 575 nm was repeated with different colour filters in the pump beam. Because the transient absorption is small, broad-band filters had to be used so the information obtained is largely qualitative. It is found that as the pump light changed from blue to red the effect changed from a drop in transmission to an increase in the transmission whereas the spectral shape remained qualitatively the same. The crossover from decrease to increase occurs at very approximately 2.5 eV. The time dependence of the transients was similar for all the filters and for white light. For white pump light the blue part of its spectrum seems to have prevailed since a decrease in transmission was seen, despite the much higher power in the red than the blue from a tungsten lamp.

The induced absorption with white light at room temperature is, not surprisingly, different from that seen by Dieleman and co-workers in ZnS : Ag with ultraviolet excitation at 77 K. Several other authors have reported changes in the optical properties of ZnS induced by illumination in a variety of experimental conditions. Because the time response and the width of the induced absorption band seen in this part of our experiments are so different from those clearly associated with manganese in the next section, these investigations were not pursued further.

3.2. Absorption induced by laser pump light

The laser light causes a fraction of the manganese centres to be in the $^4T_1(^4G)$ first excited state. From here they can decay by a luminescence transition to the ground state with the characteristic decay time ~ 1 ms. A fraction of the excited manganese centres is excited to higher excited states by the probe light, giving induced absorption. Both the luminescence intensity and the strength of the induced absorption should be proportional to the number of manganese centres in the excited state and in particular they should have the same time dependence when the pump light is chopped. This property is used
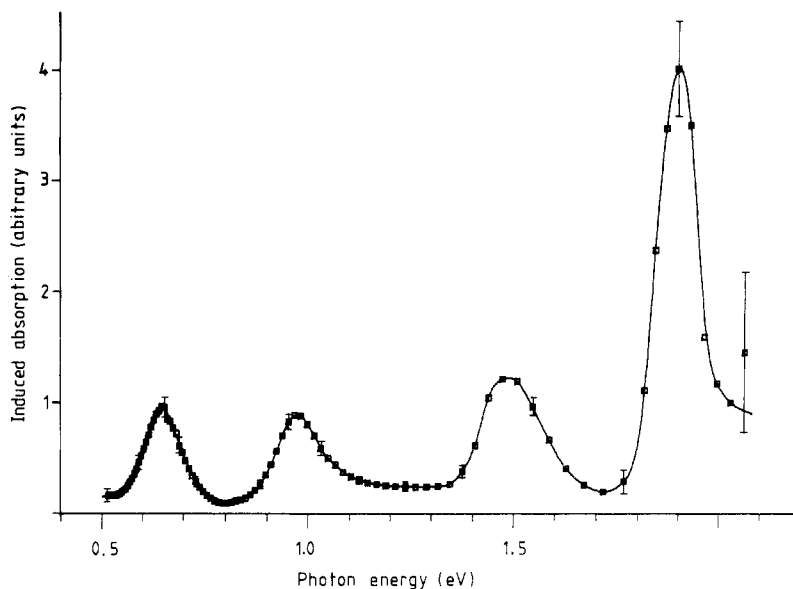
Figure 3. Spectrum between 1.5 and 3.4 eV of the absorption induced by laser light, laser light chopped at 80 Hz, phase maximised for the orange luminescence.

to determine which absorption features are directly associated with absorption within the manganese energy level scheme and which are not. Our experiments in this section fell into two parts, one the measurement of the induced absorption spectrum and the other a more detailed investigation of the time dependence via the phase of the signal. As a preliminary, the luminescence spectrum of the sample was measured and only one band was found, namely the well known $^4T_1(^4G)$-$^6A_1(^6S)$ band. The manganese concentration in the sample is in a range where the luminescent lifetime begins to vary with concentration. Inhomogeneities in the sample could therefore give spatially varying decay times. Hence in some of the experiments a second aperture at the output side of the sample was used so that the detected luminescence and absorption came, as far as possible, from the same region of the sample.

For measuring the spectrum of the induced absorption, the laser beam was chopped at 80 Hz. A reference signal from the chopper was fed to the PSD and the phase was adjusted to give maximum signal at the maximum of the luminescence at 580 nm. The probe beam was then used to measure the induced absorption with the same phase setting.

A spectral scan taken without the probe beam measures the luminescence reaching the detector, whereas with the probe beam both this luminescence and the induced absorption are measured. Hence the difference of the two scans gives the induced absorption. The spectra were normalised with respect to the transmission spectrum of the sample, which was measured in the same run by chopping the probe light. Figure 3 shows the resulting induced absorption spectrum obtained with the photomultiplier as detector in the visible and figure 4 shows that obtained in the infrared and red using a PbS cell as detector. The region 2.4–2.7 μm (0.52–0.46 eV) is not displayed: no significant feature was visible in this part of the spectrum. The spectral resolution was approximately 0.5 meV for figure 3 and 10 meV for figure 4. There are induced absorption bands at 0.65 eV with width 0.11 eV, at 0.98 eV with width 0.13 eV, at 1.49 eV with width 0.16 eV and at 1.91 eV with width 0.10 eV. The three bands at 0.65, 0.98 and 1.49 eV are of

Figure 4. Spectrum between 0.5 and 2.1 eV of the absorption induced by laser light, laser light chopped at 80 Hz, phase maximised for the orange luminescence. The vertical scale is in the same units as in figure 3.

roughly equal intensity but the 1.91 eV band is three times stronger, giving about 0.4% change in transmission. In addition there is a strong absorption starting at about 2.5 eV and rising to higher energies. The apparent drop in this feature above 3.2 eV may be an experimental artefact since here the transmittance of the crystal is small and the errors therefore large. A slight negative feature is seen in figure 4 at 2.1 eV: this corresponds with the luminescence band. Small changes of the luminescence between the two scans, caused either by the probe light or by any variation of the laser intensity, lead to a signal in this region since the luminescence is much stronger than the induced signals. Where the spectra of figures 3 and 4 overlap their agreement is good. Figure 5 shows both the induced absorption combined from figures 3 and 4 and the direct absorption. For reasons explained in § 4 the induced absorption is shifted in energy by 2.2 eV.

To test whether there were any other induced absorptions not in phase with the manganese luminescence, another spectrum was taken with the phase shifted by 90°. A broad weak band centred at about 1.2 eV was seen.

Measurements were made of the frequency dependence of the magnitude and phase of the induced absorption signal and of the luminescence signal in order to find out if the two effects have similar time dependencies. Figure 6 shows the frequency dependence of the luminescence signal and of the induced absorption at 1.91, 2.76 and 3.10 eV. The last two photon energies correspond with two points on the rising absorption feature at high energies, the first corresponds with the peak of the strongest of the induced bands. Figure 7 shows the phase shift between the induced absorption signal and the luminescence signal as a function of frequency for photon energies 0.65, 0.98, 1.49 and 1.91 eV. These energies correspond with the four peaks in the induced absorption spectrum shown in figure 4. Also shown is the phase of the very broad absorption which is centred near 1.2 eV. The accuracy of the phase angle is ±2°. Taken together, the data of figures 6 and 7 give evidence that there are four induced absorption peaks and a rising high-energy feature that are all directly associated with manganese. The phase shift and
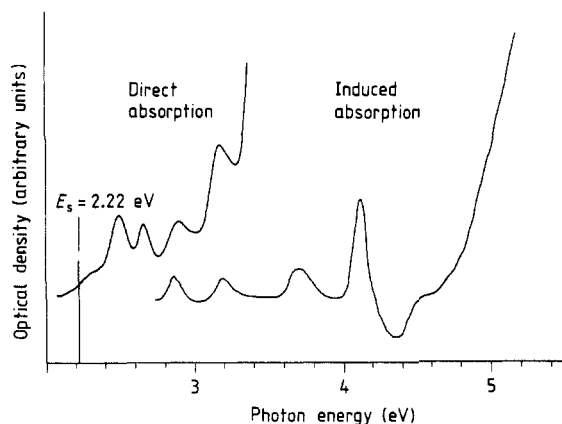
Figure 5. Direct absorption and induced absorption (figure 3 and figure 4) spectra. The latter is shifted in energy by $E_s = 2.22$ eV (energy of the ZPL of the pumped transition $^6A_1(S) \rightarrow \, ^4T_1(G)$). The zero of absorption is shifted for clarity.
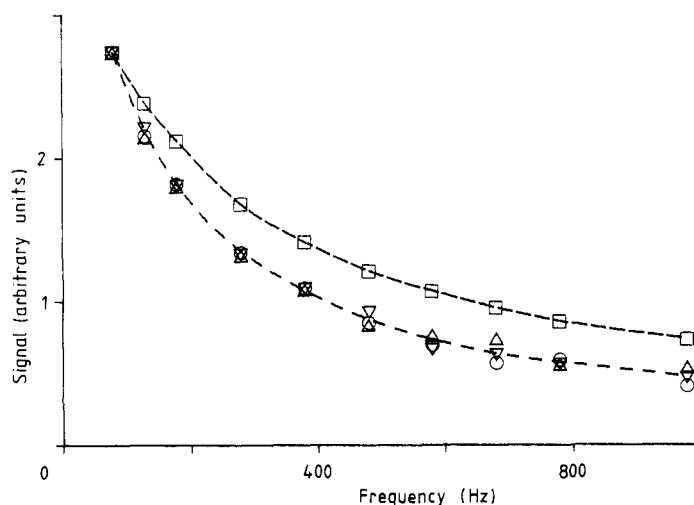

Figure 6. Dependence of the signals of the luminescence at 580 nm (2.14 eV) (□) and the induced absorption at 400 nm (3.10 eV) (∇), 450 nm (2.76 eV) (△) and 650 nm (1.91 eV) (○) on the chopping frequency. The signals were taken at the phase at which the luminescence was maximised and are normalised against their value at 80 Hz.

the small difference in frequency dependence of the magnitude of the induced absorption and the luminescence are discussed in § 4.

3.3. Luminescence with both probe and laser light

As discussed later, the induced absorption at high energies could represent photo-ionisation of the $^4T_1(^4G)$ state. If so, an electron is removed from the Mn d^5 shell and
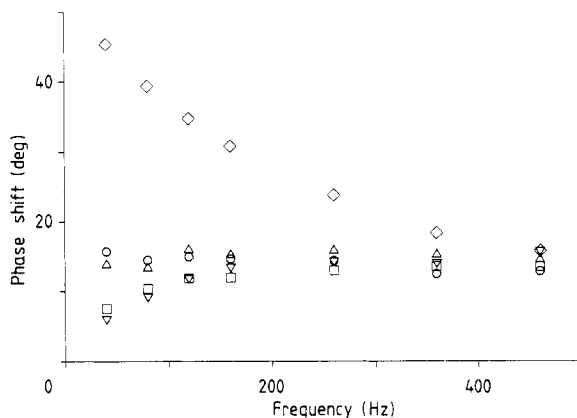
Figure 7. Phase shift of the induced absorption features at 650 nm (1.91 eV) ($\triangledown$), 830 nm (1.49 eV) ($\triangle$), 1000 nm (1.24 eV) ($\diamond$), 1270 nm (0.98 eV) ($\bigcirc$) and 1910 nm (0.65 eV) ($\square$) against the phase of the luminescence at 580 nm (2.14 eV).

then subsequently hole auto-ionisation occurs, i.e. an electron goes from the valence band to the manganese centre without change of energy. Thus, as a result of excitation to $^4T_1(^4G)$ followed by photo-ionisation, one finishes with the $Mn^6A_1(^6S)$ ground state and a free electron and hole which may recombine without involving the manganese. Photo-ionisation from a manganese centre in the $^4T_1(^4G)$ state therefore provides a quenching process since there is a mechanism of return to the ground state without the manganese luminescent transition. To test the idea, the experimental arrangement described at the end of § 2 was used. The probe light, used as the quenching light, was chopped at 80 Hz and the in-phase and out-of-phase luminescence signals were measured with the laser both on and off. In fact an in-phase signal was observed, indicating enhancement rather than quenching of the luminescence. This result does not provide evidence for or against the proposed mechanism as other mechanisms can intervene. For example, the process described in § 3.1 could have caused a laser-induced increase in transmittance, thus mimicking an enhancement of the luminescence excited by the chopped probe light. Sorting out the various possible effects would involve a very large experimental programme, so this line was not pursued further.

4. Discussion

4.1. Absorption, luminescence and white-light-induced absorption

In conventional absorption our ZnS : Mn showed the usual five absorption bands at 2.31, 2.49, 2.66, 2.90 and 3.18 eV corresponding with transitions from the ground state to the lowest excited states, and no other detectable absorption band out to 2.7 μm (0.46 eV). The luminescence spectrum was the usual manganese band peaking at 2.1 eV. White light induced a weak, very broad absorption band with slow decay time: these charac-teristics mean that this particular absorption is not seen in the conditions of the exper-iment with chopped laser pump light.

These results show that the optical properties of our sample are dominated by the presence of substitutional manganese centres. The general darkening of ZnS produced

by illumination at low temperatures (e.g. Dieleman *et al* 1964, KTO) could be neglected in our experiments, which were performed at room temperature.

4.2. Changes in absorption induced by laser light

The induced-absorption spectrum is of the form typically observed for $3d^n$ impurities in semiconductors, with a series of bands corresponding to transitions to excited states followed by an absorption rising from a threshold corresponding with photo-ionisation. Here we interpret the absorption bands induced by illumination with 514.5 nm (2.41 eV) and correlated with the manganese luminescence in phase and frequency dependence as being caused by absorption from the $^4T_1(^4G)$ first excited state of Mn d^5 to higher excited states. In this we follow KTO who saw similar induced transitions, again correlated in phase with the manganese luminescence. They used the 488 nm (2.54 eV) laser line but this difference is unimportant since excitation within any of the four normal absorption bands above $^4T_1(^4G)$ is followed by relaxation to $^4T_1(^4G)$ at a rate faster than that of the processes considered here. KTO observed the induced bands at 0.97, 1.50 and 1.89 eV seen by us (our peak values being 0.98, 1.49 and 1.91 eV) and found the same relative intensities. However they did not report the band at 0.65 eV nor the feature which rises from a threshold to higher energies. Also they gave spectra of the individual bands rather than the complete spectrum.

The fraction of excited $^4T_1(^4G)$ states in our experiment is estimated from the experimental conditions to be $\sim 7 \times 10^{-5}$. Absorption from the ground state $^6A_1(^6S)$ is spin forbidden and if the oscillator strength for the induced transitions were of the same order of magnitude then, with this excited-state population, the induced absorption would be more than an order of magnitude weaker than observed. This is evidence that the induced absorption corresponds with spin-allowed transitions to higher quartet states, as KTO have already mentioned.

The small phase shift between the induced absorption and luminescence signals, shown in figure 7, can be explained by the presence of manganese–manganese neighbouring pairs, as pointed out by KTO. The difference in frequency dependencies of the signals, shown in figure 6, has the same origin. Manganese pairs return from the first excited state to the ground state an order of magnitude faster than single manganese atoms, the lifetimes being $\simeq 0.15$ ms and 1.8 ms respectively (Busse *et al* 1976). On the other hand, absorption from $^4T_1(^4G)$ to higher quartets should have similar oscillator strengths for single and paired manganese, being spin allowed. Hence although both the luminescence and induced absorption are proportional at any instant to the $^4T_1(^4G)$ population they have different time dependencies and this leads to a phase shift. Because in our sample the fraction of paired manganese centres is small (3% if the distribution is random) the phase shift is small. It is possible to put this argument on a quantitative basis (Dreyhsig 1987). One solves the rate equations to find the variation of the induced absorption and luminescence with time and then finds the Fourier components to find the phase shift as measured by the phase-sensitive detector. We have done this for the range 20–80 Hz. In view of the numerous approximations which have to be made (e.g. neglect of energy transfer, assumption of equal oscillator strengths for induced absorption by single and paired manganese) and in view of the large experimental error in measuring the small phase shift, the agreement between theory and experiment is satisfactory. For example, at 40 Hz the calculated phase shift is 5.6° and that observed for the 1.91 eV band is 6.0 ± 3.1°. An alternative explanation of the phase shift as being due to inhomogeneities in the sample, with slightly different time constants in different
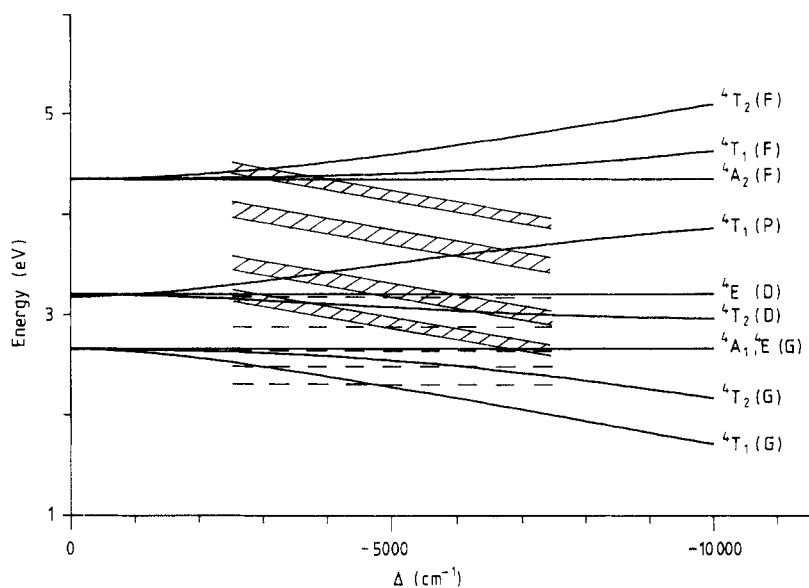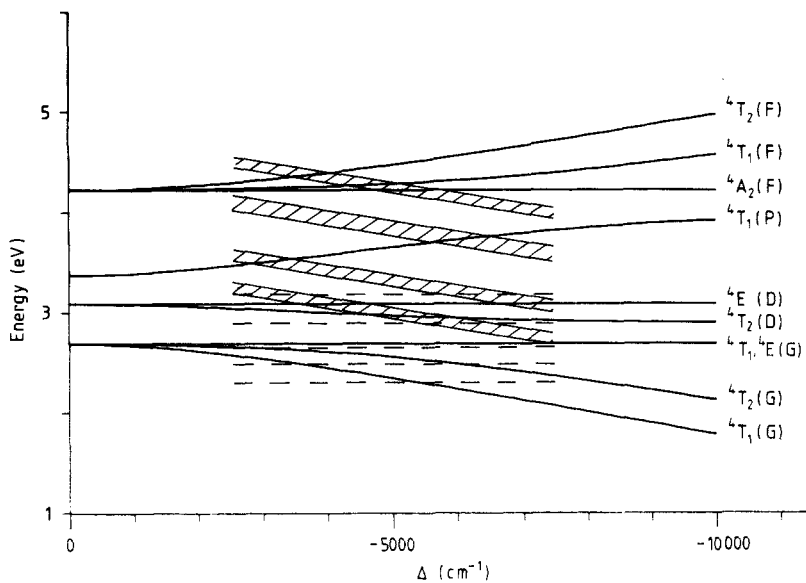
Figure 8. Tanabe–Sugano diagram of the quartet states of Mn in ZnS with Racah parameters $B = 630 \, \text{cm}^{-1}$ and $C = 3040 \, \text{cm}^{-1}$ ($C/B = 4.83$) calculated by Kushida *et al* (1974). The induced bands relative to the $^4T_1(^4G)$ state are indicated by the shaded area. The ordinary bands are represented by the broken lines where the widths are suppressed for simplicity.

regions, was discounted by using apertures to limit the excited volume of the sample giving the luminescence signals. No significant change of phase between different regions was found. The divergence of phase shifts at low frequencies between the 0.65 and 1.91 eV bands and the 0.98 and 1.49 eV bands, as seen in figure 7, is due to the perturbing effects of the broad band at 1.2 eV on the latter two bands.

Assignment of the bands to levels of particular symmetry is difficult. The ordinary absorption spectrum has five bands corresponding with five levels, of which the first three are $^4T_1(^4G)$, $^4T_2(^4G)$ and $^4E(^4G)$. Excitation by the laser is followed by relaxation to the lowest vibronic level of $^4T_1(^4G)$ or a vibronic level close to it. The starting point for the induced absorption can therefore be taken at this level, which from the zero-phonon line is 2.22 eV above the $^6A_1(^6S)$ ground state (Langer and Ibuki 1965). This is why in figure 5 the induced absorption is shown shifted in energy by 2.22 eV for comparison with the ordinary absorption. It can be seen that the first two induced bands, at 0.65 and 0.98 eV, correspond with the fourth and fifth absorption bands at 2.90 and 3.18 eV (e.g. 0.65 + 2.22 eV = 2.87 eV, 0.98 + 2.22 eV = 3.20 eV). The third induced band at 1.49 eV should correspond with an ordinary absorption band at 3.71 eV, too close to the band edge for observation. It is interesting however that Theis (1976) saw anomalies near 3.6 eV in the wavelength-modulated reflectivity of ZnS heavily doped with manganese, although he could not offer a definitive interpretation.

Customarily, the excited-state energy levels of $3d^n$ impurities are interpreted in terms of some variant of crystal-field or ligand-field theory. Many attempts have been made to do this for the five ordinary absorption bands of ZnS:Mn, without great success. Perhaps the most detailed attempt is that of Curie *et al* (1974). Because the extra information provided by the induced bands might provide a better test of the theoretical treatments we tried fitting all bands. Figures 8–10 show various possible fits using conventional crystal-field theory. Figure 8 is for the Racah parameters used by KTO,

Figure 9. Tanabe–Sugano diagram of the quartet states of Mn in ZnS with Racah parameters $B = 459$ cm^{-1} and $C = 3425$ cm^{-1} ($C/B = 7.46$) calculated by O'Neill (1984). The induced bands relative to the $^4T_1(^4G)$ state are indicated by the shaded area. The ordinary bands are represented by the broken lines where the widths are suppressed for simplicity.
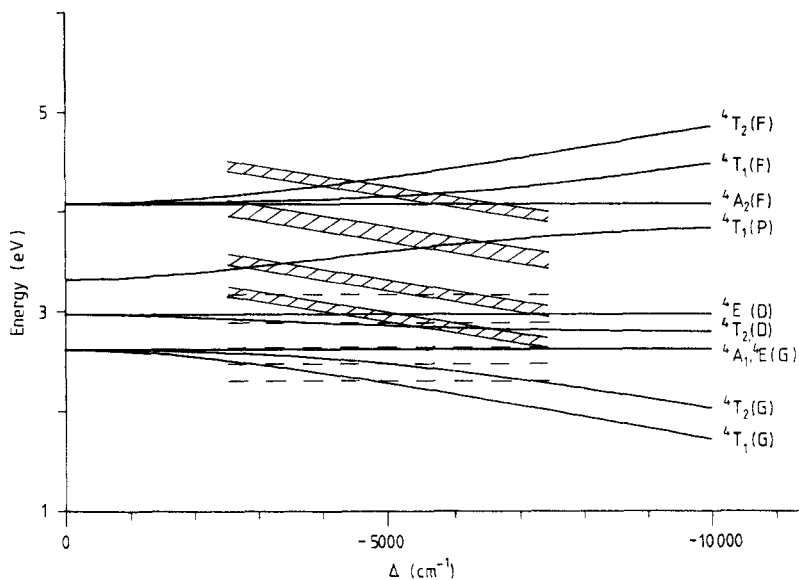
Figure 10. Tanabe–Sugano diagram of the quartet states of Mn in ZnS with Racah parameters $B = 405$ cm^{-1} and $C = 3437$ cm^{-1} ($C/B = 8.49$) calculated by Pohl *et al* (1984). The induced bands relative to the $^4T_1(^4G)$ state are indicated by the shaded area. The ordinary bands are represented by the broken lines where the widths are suppressed for simplicity.

figure 9 for those used by O'Neill (1984) based on an optimum fitting procedure for the five ordinary absorption bands, and figure 10 for those used by Pohl *et al* (1984) based with no clear justification on the position of the zero-phonon lines of the first three excited states. None yield a value for the crystal-field parameter Dq at which there is a convincing fit to the experimental data. Calculations using covalency parameters instead of reduced Racah parameters, following the methods of O'Neill and Allen (1983) or Fazzio *et al* (1984), give no substantial improvement. This is not totally surprising in view of the numerous approximations which have to be made in any usable theory, e.g. the same Racah or covalency parameters for all levels. Also the lattice relaxation is unusually large in ZnS:Mn, and the widths of the bands show that it cannot be taken to be the same for all the quartet states, an effect ignored in the theory. (It should be pointed out that the width of the induced quartet–quartet bands are similar to those of the ordinary sextet–quartet bands, so the unusually large widths are not due to relaxation of the spin selection rule by phonons via the spin–orbit interaction.)

By analogy with the spectra of other $3d^n$ impurities, the obvious interpretation of the induced-absorption feature at higher energies is that it corresponds with photo-ionisation from the $^4T_1(^4G)$ level to the conduction band. If the phonon interaction is not too strong, the absorption near threshold varies as $(h\nu - E_1)^{3/2}$, where E_1 is the ionisation energy, specifically the vertical energy in a configurational coordinate diagram. Using this, the experimental data of figure 3 give an ionisation energy 2.4 eV. Since the band gap of ZnS at room temperature is 3.7 eV and the $^6A_1$–$^4T_1$ spacing is 2.2 eV, this puts the level for removing an electron from the $^6A_1$ ground state at 0.9 eV below the valence band edge. The uncertainty is large, about ± 0.3 eV, because of the effects of the different lattice relaxations for the different states. An early semi-empirical method by Allen (1964) put the level about 0.3 eV above the valence band edge, but this is not reliable as the data available at the time, from which the interpolation was made, were extremely sparse. The improved method of Fazzio *et al* (1984), with improved experimental data from which to interpolate, puts the level 0.7 eV below the valence band edge, in good agreement with our result.

Experimental tests to find whether this high-energy feature really is associated with photo-ionisation are difficult to devise. For example, the usual tests of change of charge state such as photocapacitance or photo-ESR are unlikely to work, since once an electron has been removed from a manganese centre by photo-ionisation the charge state is expected to be restored rapidly by capture of an electron from the valence band. At first sight, an interpretation in terms of photo-ionisation is contrary to the findings of photo-emission experiments, in which a set of manganese-related levels are observed at about 3 eV below the valence band edge in some II–VI compounds. Unfortunately early photo-emission experiments on the II–VI compounds were often erroneous because insufficient precautions were taken to eliminate matrix element and surface effects and there are no recent reliable results for ZnS:Mn. In the work by Langer *et al* (1970) on x-ray photo-emission of ZnS:Mn a small difference in the shape of the valence band spectrum was seen between crystals with and without 3% manganese but the experimental error was too large for definitive evidence of a manganese band in this energy range to be obtained. The x-ray source they used had a linewidth of 0.9 eV so the levels we see would not be expected to be resolved from the rest of the valence band in their experiments. It would be valuable if the photo-emission experiment were to be repeated with modern techniques. However, even if there are manganese-related states in a band ≈ 1 eV wide at about 3 eV below the valence band edge this is not necessarily in contradiction with our interpretation. Bonding between the manganese and the host crystal can be treated

as a hybridisation of states. In a lowest approximation the Mn t_2 orbitals hybridise with t_2 ligand orbitals producing two manganese-related levels, one bonding and one anti-bonding. In a higher approximation there will be a band of levels associated with host levels perturbed by the presence of manganese, and manganese levels perturbed by the host. Observation of one kind of level in one type of experiment does not preclude the possibility of observing the other in another type of experiment.

5. Conclusions

The absorption spectrum for transitions starting from the first excited state of ZnS:Mn consists of four bands followed by a feature rising from a threshold to higher absorption at higher energies. The first two bands correspond with the fourth and fifth bands seen in ordinary absorption from the ground state. None of the available theories with a tractable number of parameters gives a satisfactory fit to the experimental data. The rising feature at higher energies is interpreted as being due to photo-ionisation from the first excited state to the conduction band. This places the level of ionisation from the ground state of ZnS:Mn at 0.9 ± 0.3 eV below the top of the valence band.

Acknowledgments

References

Allen J W 1964 *Proc. 7th. Int. Conf. Physics of Semiconductors (Paris) 1964* (Paris: Dunod) p 781
Busse W, Gumlich H-E, Meissner B and Theis D 1976 *J. Lumin.* **12/13** 693
Curie D, Barthou C and Canny B 1974 *J. Chem. Phys.* **61** 3048
Dieleman J, van Doorn C Z, de Bruin S H and Haanstra J H 1964 *Proc. 7th Int. Conf. Physics of Semiconductors (Paris) 1964* (Paris: Dunod) p 941
Dreyhsig J 1987 *MSc Thesis* University of St Andrews (unpublished)
Fazzio J, Caldas M J and Zunger A 1984 *Phys. Rev.* B **30** 3430
Goede O and Heimbrodt W 1988 *Phys. Status Solidi* b **146** 11
Gulmlich H-E 1981 *J. Lumin.* **23** 73
Kröger F A 1939 *Physica* **7** 369
Kushida T, Tanaka Y and Oka Y 1974 *J. Phys. Soc. Japan* **37** 1341
Langer D and Ibuki S 1965 *Phys. Rev.* **138** A809
Langer D W, Helmer J C and Weichert N H 1970 *J. Lumin.* **1/2** 341
O'Neill A G 1984 *PhD Thesis* University of St Andrews (unpublished)
O'Neill A G and Allen J W 1983 *Solid State Commun.* **46** 833.
Pohl U W, Gumlich H-E and Busse W 1984 *Phys. Status. Solidi* b **125** 773
Theis D 1976 *Phys. Lett.* **59A** 154