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Temperature Dependence of the Absorption Edge in $Cd_{1-g}Mn_gSe$

By

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$Cd_{1-g}Mn_gSe$ is a new material which forms homogeneous single crystals with the wurtzite structure /1, 2/ in the range $0 < g < 0.45$. These crystals are n-type, usually high resistivity, large gap semiconductors. The recent interest in this material derives from the presence of the paramagnetic Mn^{2+} ion in the lattice /3/.

Early optical absorption measurements /4/ performed at liquid nitrogen and room temperatures indicate a linear dependence of the energy gap with composition in the range $0 < g < 0.34$. We have extended these measurements to cover a wider range of temperatures and higher Mn concentrations. In this way we obtain accurate values for the temperature coefficient of the absorption edge as a function of Mn concentration and describe its temperature dependence for higher Mn contents. The high composition data provides interesting new information about the optical absorption mechanism in $Cd_{1-g}Mn_gSe$. An absorption process, different from the direct valence to conduction band excitation responsible for the absorption at low values of g, is identified for $g > 0.35$. This process is similar to the one we discussed for $Cd_{1-x}Mn_xTe$ in a previous work /5/, assigned to excitations probably due to a Mn derived band in the gap.

The crystals were grown by a modified Bridgman method using high purity initial materials. The Mn content of the samples was determined by atomic absorption in an EPR apparatus /6/; density measurements showed a linear variation with composition from 5.64 g/cm^3 for $g = 0.0$ to 5.04 g/cm^3 for $g = 0.45$. The samples were cleaved along a plane parallel to the c axis, and polished to a thickness of 1 mm. The absorption edge spectra were recorded in a Cary 17DI spectrophotometer in the energy range 1.6 to 2.4 eV. The instrument records the optical density. By choosing a constant sample width, we

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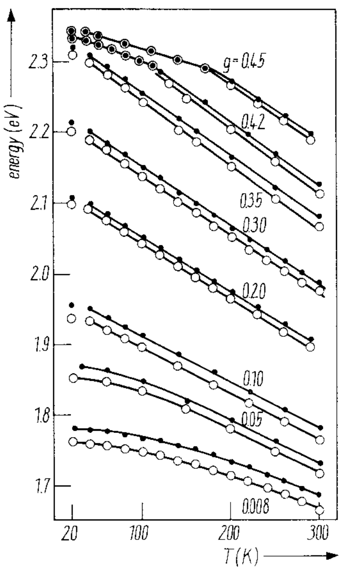

Fig. 1. Position of the absorption edge as a function of temperature for various sample compositions. The measurements were made in the directions $\vec{E} \parallel \vec{c}$ (●) and $\vec{E} \perp \vec{c}$ (○)

obtain a family of curves proportional to the absorption edge with the same arbitrary scale factor. The samples were mounted on the cold finger of a Displex refrigerator for temperature dependent measurements at 20 K intervals from 20 K to room temperature. Orientation of the polarization vector of the incident light allowed us to sample the selection rules for the various transitions observed. The background absorption is estimated at 3 cm^{-1}, while the maximum measured absorption on the 1 mm samples was about 60 cm^{-1}. The position of the absorption edge is parametrized by the energy corresponding to maximum absorption. The line shapes were analyzed with a least squares fit to the data.

No band structure calculations of $Cd_{1-g}Mn_gSe$ have been reported. However, we can give a qualitative description of the optical absorption process by considering the band structure of CdSe. The absorption edge is associated with direct transitions at the Γ point from the crystal field split valence band to the conduction band. The selection rules are such that transitions from the upper branch ($\Gamma_9 \rightarrow \Gamma_7$) are allowed for the polarization of the incident light in the direction $\vec{E} \perp \vec{c}$, while the transitions from the lower branch and from the spin-orbit split valence band ($\Gamma_7 \rightarrow \Gamma_7$) are allowed for $\vec{E} \perp \vec{c}$ and $\vec{E} \parallel \vec{c}$. In the last case the direction $\vec{E} \parallel \vec{c}$ is dominant.

Fig. 1 shows the temperature dependence of the absorption edge. Two curves are given for each composition corresponding to the two polarizations. The crystal field splitting, estimated from the separation of the two curves for each particular composition, is about 20 meV for small compositions and decreases to 10 meV for $g = 0.45$.

The energy gap for CdSe can be estimated from the absorption edge by means of the empirical Urbach's rule /7, 8/. This analysis is also applicable

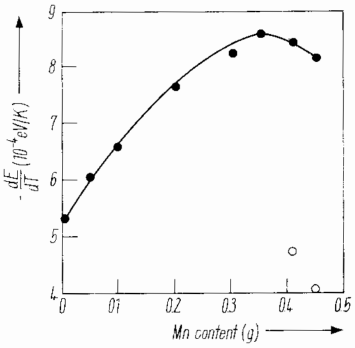

Fig. 2. Temperature coefficient of the absorption edge. The dots represent the slopes of the $\vec{E} \parallel \vec{c}$ curves in Fig. 1. The circles correspond to the slopes of the low temperature sides of the g = 0.42 and g = 0.45 curves

to the data for samples with low Mn content, where the absorption edge is exponential. The method becomes less accurate as g increases, since the shape of the absorption edge gradually departs from the simple exponential form. The absorption edge varies linearly with composition in the high temperature range (T > 200 K) for all the samples studied. This resembles the dependence of the energy gap on composition for a given temperature as a result of electroreflectance /9/ and photoluminescence /1/ measurements: our results are consistently about 70 meV below the corresponding value of the energy gap. A different dependence is observed in the low temperature regions of the g = 0.42 and g = 0.45 curves in Fig. 1. For these cases, the absorption is independent of polarization and has a different temperature variation compared with the high temperature sides of the same curves. The temperature at which this change in temperature dependence occurs is well defined: 110 K for g = 0.42 and 170 K for g = 0.45. This behavior is not observed in photoluminescence experiments.

A numerical analysis of the absorption edge line shape showed a departure from the simple exponential form with higher Mn content. This effect is more pronounced near the region where a strong change in the temperature coefficient is observed, and seems to indicate that the absorption edge line shape is affected by a strong transition other than the direct interband transition which dominates the low Mn concentration data.

Fig. 2 shows the temperature coefficient of the absorption edge obtained from the data in Fig. 1. It varies from -5.3×10^{-4} eV/K for g = 0.01 to -8.6×10^{-4} eV/K for g = 0.35. For the two highest values of g, the temperature coefficient shows a decrease from the maximum at g = 0.35. The values obtained from the low temperature measurements on the same two samples are shown in Fig. 2.

Our experiments give a detailed description of the temperature dependence of the absorption edge for $Cd_{1-g}Mn_gSe$. A break in the temperature dependence of the high Mn content samples, not previously observed in optical or electroreflectance experiments, indicates that in these cases the optical absorption is not dominated by direct valence to conduction band transitions. This new absorption process is not likely to be due to ionic excitations of the Mn^{2+} 3d states. We base our conclusion on the observed strength of the excitation which competes with the direct valence to conduction band transitions at Γ. Ionic excitation of the d levels is not allowed in first order, and is observed as weak absorption peaks, of the order of our background, in compounds such as $KMnF_3$, with very little temperature dependence /10/. The transitions observed here are strong, comparable to the interband excitations observed for low Mn contents, and show a high temperature dependence (greater than $-4x10^{-4}$ eV/K). We are probably observing a Mn derived band which comes below the band gap at low temperatures for high values of g.

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