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Anisotropy of optical absorption in wurtzite-phase $Zn_{0.85}Mn_{0.15}S$

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Optical-absorption results on single-crystal samples of wurtzite-phase $Zn_{0.85}Mn_{0.15}S$ are reported. Five absorption bands associated with the Mn^{2+} intraion transition are seen. Polarization results for the four lowest bands are found to be similar to previous observations in wurtzite-phase $Zn_{1-x}Mn_xSe$, indicating systematic polarization in the Zn-based dilute magnetic semiconductors.

I. INTRODUCTION

In a recent paper,[1] we reported on optical absorption of the dilute magnetic semiconductor (DMS) $Zn_{1-x}Mn_xSe$. The investigation revealed the first evidence for polarization effects in the broad Mn^{2+} intraion transitions for samples in the wurtzite region ($0.3 \lesssim x < 0.57$). These results are of interest since extended x-ray-absorption fine structure (EXAFS) suggests that distortion of the local environment of Mn from T_d occurs in ternary alloys of $Zn_{1-x}Mn_xSe$.[2] In our work, an explanation for the polarization was sought based on the model of a bimodal distribution of Mn—Se Zn—Se bond lengths and the splitting of Mn^{2+} $3d^5$ states due to bond bending. Applications of this model for a random distribution of Mn in the lattice suggested instead that no polarization should be present in any band, even in the C_{3v} wurtzite phase.

In order to clarify this question, we have extended the investigation to include study of the polarization effects in $Zn_{1-x}Mn_xS$, a second Zn-based DMS which can be grown in the wurtzite phase. The width of the band gap in this material[3] (~ 3.7 eV) as compared to the selenide[4] (~ 3.0 eV) gives a special opportunity for determining the behavior of several higher Mn transitions which are inaccessible in the lower gap material at atmospheric pressure. Choice of x values for investigation was made based on phase diagram information for the ZnS-MnS system,[5] available samples, and interest in comparing the broad band features in the two materials.

II. EXPERIMENT

The monocrystals used in this study were grown by the chemical vapor transport method.[6] Single crystals of external hexagonal morphology and good optical quality were chosen for study. The wurtzite structure was confirmed by x-ray measurements. The crystals were cut and oriented with the **c** axis in the plane of the polished surface. Two samples of different thickness were required to cover the spectral region investigated: thicknesses chosen were 87.5 ± 1 and 370 ± 1 μm. The sample thicknesses were measured interferometrically. Adjacent slices of the same crystal were used to ensure that they had the same manganese concentration. The manganese composition was determined to be $x \cong 0.15\pm0.005$ by microprobe analysis. Sample preparation techniques and measurement procedures are identical to those described previously in the $Cd_{1-x}Mn_xSe$ alloy system.[7]

III. RESULTS

Absorption coefficients were calculated using the formula appropriate for multiple reflections at normal incidence for samples with parallel faces,

$$T=\frac{(1-R)^2e^{-\alpha t}}{1-R^2e^{-2\alpha t}}$$

where T is the fraction of transmitted light, t is the sample thickness, α is the absorption coefficient, and R is the sample reflectance.

The above equation yields the absorption coefficient, provided the reflectance is known as a function of wavelength. Published values for the reflectance of $Zn_{1-x}Mn_xS$ are not yet available in the literature. The reflectance of ZnS has been measured[8] to vary from ~ 0.27 to ~ 0.30 in the range from ~ 2.0 eV to ~ 3.0 eV. Unfortunately, these values for R yield negative absorption coefficients below the Mn threshold ($E < 2.2$ eV) in our samples. Instead the reflectance was derived by using two samples of the same manganese concentration but of different thickness; the value of R was then adjusted until both samples gave the same absorption coefficient at the same wavelength. In our work R was chosen to match the absorption coefficients of the 370-μm sample and the 87.5-μm sample at 515 nm. This wavelength was chosen because it lies in the midrange of the onset of the Mn^{2+} absorption threshold, where both samples showed significant absorption ($\alpha \sim 23$ cm^{-1}). To obtain a good match, it was found that different values of R were necessary for different polarization directions. Optimum agreement was obtained for E∥c using $R_{\parallel}=0.10$ and E⊥c using $R_{\perp}=0.153$. These choices are consistent with the earlier work on $\mathrm{Zn}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ (Ref. 1) where the difference in $R_{\perp}$ ($R_{\parallel}$) with E-field direction gave the trend $R_{\perp}>R_{\parallel}$.[1] Changes of the index of refraction of ZnS have been shown to be less than 10% in the spectral range of interest;[9] as a result, no dispersion in the value of $R_{\perp}$ ($R_{\parallel}$) was used in calculating the absorption coefficient. We note, however, that the $R_{\perp}$ ($R_{\parallel}$) values chosen above gave a mismatch of the absorption coefficients for the thick and thin samples at the shorter wavelengths, possibly indicating some dispersion in $R_{\perp}$ ($R_{\parallel}$). As a consequence, the sign of the polarization is uncertain for the highest-energy Mn absorption band found.

Figure 1 gives absorption spectra ranging from the Mn threshold to within $\sim 0.2-0.3$ eV of the band edge for E∥c at 19, 83, and 293 K. The sharp rise in α beyond $E \sim 3.4$ eV at 293 K suggests the onset of band to band absorption, found at ~ 3.6 eV for $x \sim 0.15$ (Ref. 3). Expected thermal shifts of this edge to higher energy could not be studied because of low source strength in the near-uv region. As seen in the figure, five distinct bands emerge with decreasing temperature, with the magnitude and position independent of temperature. Figure 2 gives the absorption in the Mn region for both directions of E field at 19 K. The assignments of the bands, as given in Fig. 2, are according to the theoretical results and discussion of Richardson and Janssen.[10] We note that some disagreement has existed about the assignment of the fourth and fifth bands to $b\,^4T_2$ and $b\,^4T_1$, respectively. Intensities of excitation to the nearly degenerate $a\,^4A_1(^4G)$ and $a\,^4E(^4G)$ levels estimated by Parrot and Blanchard[11] are such that only $a\,^4E$ should contribute significantly to the third band.

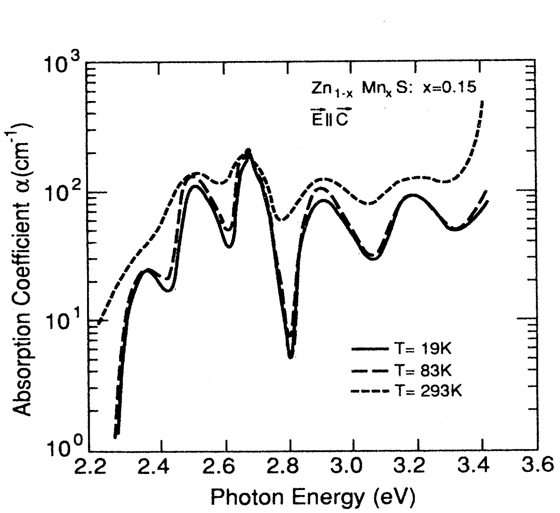

FIG. 1. Absorption spectra for E∥c at 19, 83, and 293 K.

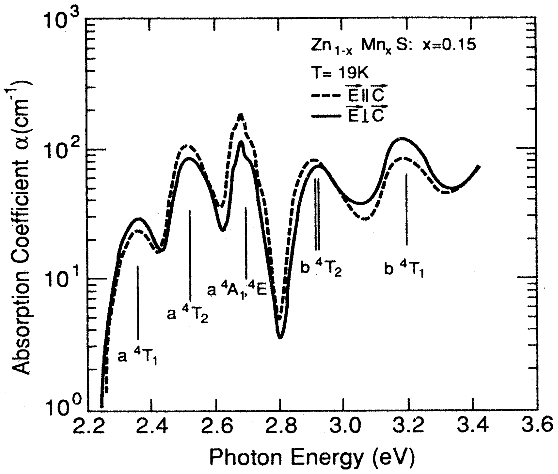

FIG. 2. Absorption spectra for E∥c and E⊥c at 19 K.

IV. DISCUSSION

Polarization features in the manganese absorption spectra reported here are similar to those observed in the wurtzite phase of $\mathrm{Zn}_{1-x}\mathrm{Mn}_x\mathrm{Se}$.[1] For the $a\,^4T_1$ transition (at ~ 2.35 eV), $\alpha(\mathbf{E}\perp\mathbf{c})>\alpha(\mathbf{E}\parallel\mathbf{c})$, while in the $a\,^4T_2$ and $a\,^4A_1,^4E$ transitions (at ~ 2.5 and ~ 2.68 eV, respectively) $\alpha(\mathbf{E}\parallel\mathbf{c})>\alpha(\mathbf{E}\perp\mathbf{c})$. The $b\,^4T_2$ transition (at ~ 2.9 eV) shows a small splitting with $\alpha_{\max}(\mathbf{E}\parallel\mathbf{c})$ at lower energy ($\Delta E \sim 0.02$ eV) than $\alpha_{\max}(\mathbf{E}\perp\mathbf{c})$, similar to the behavior of the same transition in the selenide. In turn, the present result strengthens the earlier observation since band-edge overlap effects which may contribute to the $b\,^4T_1$ band shape in the selenide are not a problem in the sulfide.

Work by McClure and others[12,13] shows that in DMS's, narrow features, i.e., zero phonon lines, phonon sidebands, pair spectra, etc., in optical absorption or excitation of Mn disappear for $x \gtrsim 0.1$. We note residual structure in the $a\,^4A_1,^4E$ transition at 19 K, including a peak at ~ 2.68 eV, and shoulders at ~ 2.56 and ~ 2.71 eV; these are similar to features seen by McClure in $\mathrm{Zn}_{0.95}\mathrm{Mn}_{0.05}\mathrm{S}$ (cubic) at 77 K.

The current results, together with the earlier reported work on $\mathrm{Zn}_{1-x}\mathrm{Mn}_x\mathrm{Se}$, suggest that a given pattern for the polarization of absorption holds for the broad Mn d-d intraion transition in Zn-based wurtzite-phase DMS's. It is unlikely that still higher bands may be observed in the sulfide because of the known band-gap closure with increasing x.[3] We note that of the DMS's with wurtzite structure, only $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{S}$ has a sufficiently wide band gap to study the three lowest transitions in Cd-based systems.[14]

ACKNOWLEDGMENTS

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