TEMPERATURE DEPENDENCE OF THE ABSORPTION EDGE IN $Cd_{1-x}Mn_xTe$

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The optical absorption of $Cd_{1-x}Mn_xTe$ crystals was measured as a function of temperature and Mn content. The negative temperature coefficient, independent of Mn content for $x > 0.4$, is discussed in terms of possible absorption mechanisms different from the interband transitions which dominate the absorption for lower Mn concentrations.

$Cd_{1-x}Mn_xTe$ crystals form homogeneous solid solutions with the zinc-blende structure in the composition range $0 \leqslant x \leqslant 0.7$, behaving as large gap semiconductors. These compounds are particularly interesting because of their unusually large magneto–optical effects caused by the presence of the paramagnetic Mn^{2+} ions in the lattice [1,2]. The possibility of tuning the enrgy gap by means of an applied magnetic field, temperature variation, and Mn content may lead to future applications.

We have done a systematic study of the optical absorption as a function of temperature and Mn content and obtained the temperature coefficient of the absorption edge. Previous optical absorption experiments performed on these crystals at room and liquid nitrogen temperatures suggest that for $x \gtrsim 0.5$ the Mn^{2+} 3d states are responsible for the absorption [3]. An analysis of our data and its comparison with other optical experiments led us to the conclusion that *localized* ionic excitation is not the mechanism most likely to dominate the absorption at high Mn concentrations.

The experiments were performed on a set of ten $Cd_{1-x}Mn_xTe$ single crystals, grown by a modified Bridgman method, mechanically cut and polished to thicknesses of about 1 mm. The Mn content of the samples, in the range $0 \leqslant x \leqslant 0.7$, was determined by atomic absorption. Sample cooling was achieved by placing the crystals in a copper block attached to the cold finger of a Displex refrigerator. The optical absorption spectra were recorded at 20 K intervals in the temperature range $20 \lesssim T \lesssim 300$ K, using a Cary 17DI spectrophotometer. All the measurements were done under the same conditions in order to facilitate the comparison of the various absorption spectra. In our estimate, the background absorption at low ener-

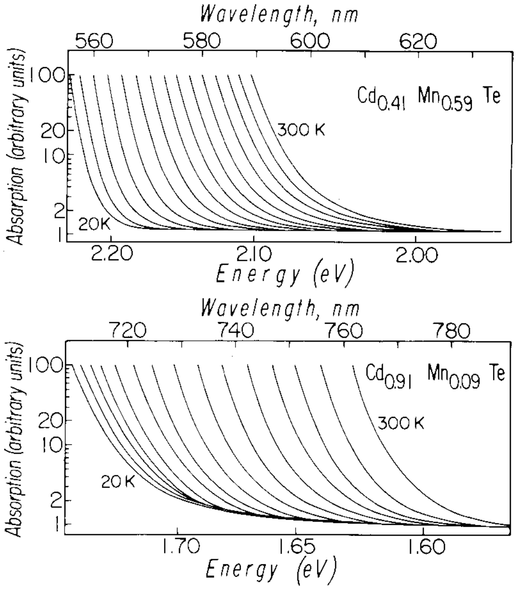

Fig. 1. Typical absorption spectra corresponding to samples with high and low Mn content measured at 20 K temperature intervals.

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gies (due to free carriers, defect scattering, etc.) was about 3 cm^{-1}.

Fig. 1 shows two typical sets of absorption curves, corresponding to samples with low and high Mn content. An analysis of the absorption curves showed that for $x \lesssim 0.4$ the absorption edge does not have an exponential line shape. Therefore, it was not possible to use Urbach's rule [4] to parametrize our line shapes in a manner analogous to previously reported data [3]. We noticed, however, that for $x > 0.4$ the absorption edge is approximately exponential. We chose the energies corresponding to the maximum absorption recorded (approximately 60 cm^{-1}) as a measure of the positions of the absorption edges. A graph of these energies as a function of temperature is shown in fig. 2 for all the samples studied.

For low Mn concentrations ($x \lesssim 0.3$), direct interband transitions at the Γ point dominate the absorption spectrum: the energies are in good agreement with those obtained by electroreflectance [5] and photoluminescence [6] measurements. The transition energies associated with the band gap, plotted as a function of x, can be fitted to a straight line up to $x \approx 0.3$. As more Mn is added to the lattice, the absorption energies deviate from the expected behavior. In particular, for $x > 0.5$, the absorption energies are independent of x, whereas the direct band gap continues to increase [5,6]. This saturation is clearly seen in fig. 3 for four different temperatures. A mechanism other than direct interband transitions dominates the absorption for high Mn content [3], as we discuss below.

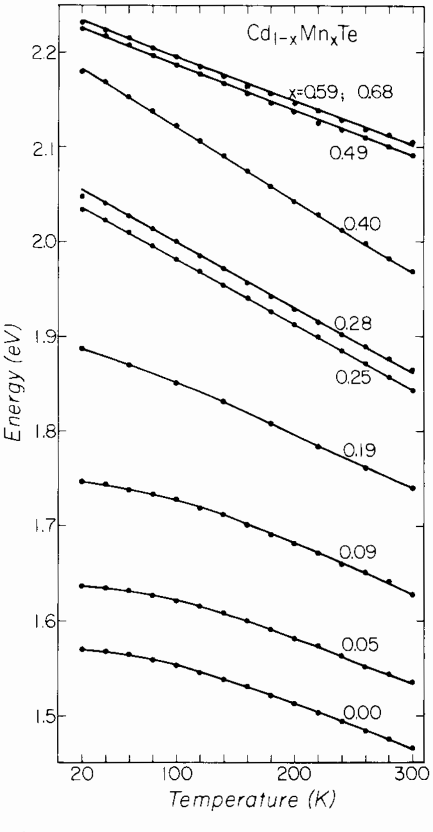

Fig. 2. Absorption edge positions as a function of temperature for various sample compositions.

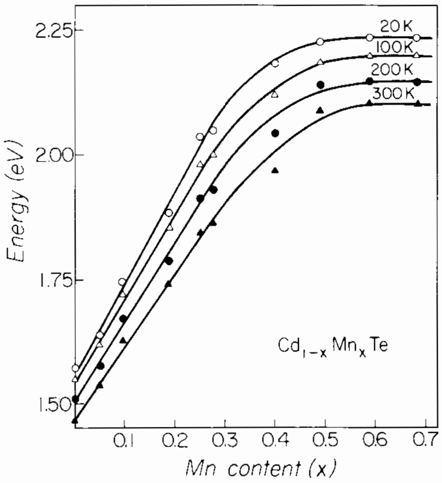

Fig. 3. Position of the absorption edge as a function of Mn content x for four different temperatures.

The temperature coefficient of the absorption edge as a function of Mn concentration is shown in fig. 4. Two curves are presented to illustrate the non-linearity of the temperature variation shown in fig. 2 for $x \lesssim 0.3$. Curve A is a linear fit to the high temperature data (above 180 K), while curve B represents a fit to the low temperature region (below 80 K). As x increases, the temperature dependence of the absorption edge becomes increasingly high, reaching values rather large for a typical semiconductor [5]. The change of the direct gap with temperature could be related to changes in the lattice phonon frequency. This could occur when Mn is added to the CdTe lattice, causing the formation of vacancy sites around which electrons and holes can be trapped, leading to a softening of the normal-mode frequency of the lattice [7]. As x increases further, a discontinuity in the

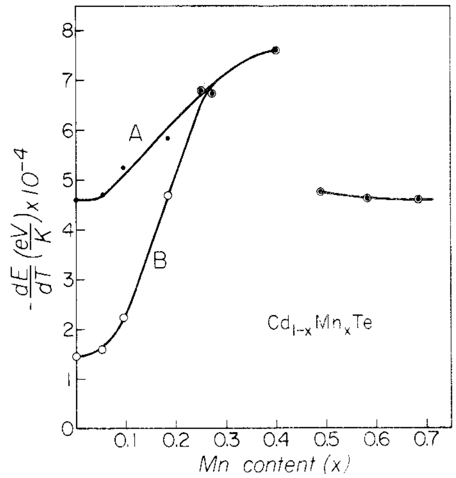

Fig. 4. Temperature coefficient as a function of Mn content x. Curve A is a fit to the data shown in fig. 2 for temperatures above 180 K. Curve B is a fit in the region below 80 K.

temperature coefficient appears at $x \approx 0.45$, when direct interband transitions are no longer the dominant effect. It is seen from fig. 4 that for high Mn concentrations the temperature coefficient saturates, but its magnitude is still large, of the order of -4.6×10^{-4} eV/K.

It has been proposed that for $x \gtrsim 0.5$, the optical absorption is caused by transitions within the Mn^{2+} ions [3]. It is well known that concentrated Mn compounds such as MnF_2, $RbMnF_3$, etc. show an absorption due to the Mn^{2+} ^4G excited level [8] at about 2.3 eV, an energy close to that of the $Cd_{0.4}Mn_{0.6}Te$ absorption edge. However, the ionic absorption observed in those compounds is of the order of our background (about 3 cm^{-1}), and it seems unlikely that it could cause the strong absorption coefficients (greater than 100 cm^{-1}) measured in $Cd_{1-x}Mn_xTe$. Also, the temperature coefficient is too large to be associated with ionic excitations and it is of the wrong sign (the lowest Mn^{2+} excited state is expected to shift to lower energies with increasing crystal field [9] as the temperature decreases). Furthermore, photoconductivity measurements performed on a $Cd_{0.4}Mn_{0.6}Te$ sample showed a peak at the absorption edge energy [10].

The evidence suggests that the Mn could still be responsible for the absorption, possibly through a Mn d-band appearing at a lower energy than the conduction band of the material for high Mn concentrations. A similar effect is observed in MnTe [11], where the absorption edge is thought to arise from charge transfer transitions between the Te p-derived valence band and Mn 3d states in the gap. Another possible explanation would be the occurrence of a conduction band minimum away from Γ as x increases. The absorption edge would then be related to non-vertical transitions.

Further work is required for a better understanding of the $Cd_{1-x}Mn_xTe$ system. Absorption experiments on thin samples could allow us to observe the direct gap measured elsewhere [5,6] at around 2.5 eV, and possibly the Mn^{2+} absorption at a lower energy. A study of the absorption edge in the presence of a magnetic field could yield useful information on the nature of the absorption mechanisms.

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