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LETTER TO THE EDITOR

Temperature and composition dependence of the energy gap in $Cd_{1-x}Co_xSe$

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Abstract. Wavelength-modulated reflectivity spectra near the fundamental absorption edge of $Cd_{1-x}Co_xSe$ ($0.01 \leqslant x \leqslant 0.053$) solid solutions have been obtained at temperatures between 8 and 250 K. A line-shape analysis of the structures observed allows us to determine the temperature and composition dependence of interband transition energies. The energy gap varies linearly with composition in the range studied. The temperature variation of the energy gap can be fitted well by the empirical Varshni relation.

The $Cd_{1-x}Co_xSe$ alloys belong to the class of diluted magnetic semiconductors (DMS) in which the magnetic atoms (Mn, Fe, Co) randomly substitute the group II atoms of the host II–VI semiconductor (e.g. CdSe). DMS have attracted attention for several reasons [1]. Their magnetic properties arising from the disordered nature of the magnetic sublattice are interesting and they show novel physical effects related to the exchange interaction between localized moments and band electrons. The possibility of controlling the energy gap and other physical parameters of DMS by varying the composition is important as well. Recently, results of electron Raman scattering [2], magnetic susceptibility [3,4], magnetoreflectance [5,6], magnetization [6] and neutron scattering [7] in Co-based DMS have been reported. However, no systematic studies of the variation of the energy gap with composition and temperature in these alloys have been performed until now.

In this communication we report how the energy gap of the $Cd_{1-x}Co_xSe$ system varies both with composition ($0 < x \leqslant 0.053$) and with temperature ($8\ K \leqslant T \leqslant 250\ K$). We find that the energy gap varies linearly with composition in the range studied. The temperature variation of the energy gap is fitted well by the empirical Varshni formula.

The $Cd_{1-x}Co_xSe$ ($0 \leqslant x \leqslant 0.1$) single crystals which were studied were grown using a modified Bridgman method. Their composition, x, was checked by atomic absorption analysis. The values of x, within an experimental error of 10%, were close to the theoretical (nominal) composition in all cases. X-ray diffraction studies show that the $Cd_{1-x}Co_xSe$ crystals have a hexagonal structure.

Single crystals of good optical quality were obtained for $x \leqslant 0.06$. We measured wavelength-modulated reflectivity (WMR) on six samples for various values of the

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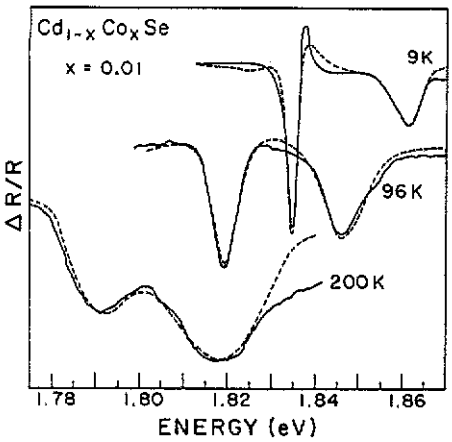

Figure 1. WMR spectra for $Cd_{0.99}Co_{0.01}Se$ at different temperatures. The dashed curves are the best fits to the experimental curves.

composition in this range. The normalized derivatives of the sample reflectivity were obtained in the temperature range from 8 K to 250 K using a near-normal-incidence reflectometer.

Figure 1 shows typical WMR spectra for $Cd_{0.99}Co_{0.01}Se$ at three different temperatures. Two peaks are observed in the spectra of all samples. The lower-energy structure corresponds to the transition from the top valence band Γ_9 to the conduction band (A exciton) and the higher one to the transition from the crystal-field-split Γ_7 valence band to the conduction band (B exciton). This assignment has been corroborated by our measurements with polarized light.

The experimental line shapes have been analysed using the expression given by Aspnes [8], which relates the change in the reflectivity, $\Delta R/R$, to the perturbation-induced change in the complex dielectric constant, $\Delta\epsilon$,

$$\Delta R/R = \mathrm{Re}[C\exp(\mathrm{i}\phi)\Delta\epsilon] \tag{1}$$

where C and ϕ are an amplitude and the phase angle, respectively. The contribution of an excitonic discrete level at energy E_0 to the dielectric constant is given by [9]

$$\epsilon \propto [(E_0 - E) - \mathrm{i}\Gamma]^{-1} \tag{2}$$

where Γ is the Lorentz broadening parameter ($\Gamma \ll E_0$). The amplitude C, threshold energy E_0, broadening parameter Γ and phase angle ϕ were determined by fitting the numerically obtained first-derivative spectra of ϵ to the experimental WMR data. The dashed curves shown in figure 1 are the best fits to the experimental curves.

Figure 2 exhibits the obtained composition dependence of the A exciton energy in the $Cd_{1-x}Co_xSe$ samples. The energy E_0 (the energy gap less than the exciton binding energy) varies linearly with composition in the range studied. A least squares fit gives

$$\begin{aligned} E_0(x) &= 1.779 + 1.025x \quad &&\text{at 200 K} \\ E_0(x) &= 1.808 + 1.060x \quad &&\text{at 100 K} \\ E_0(x) &= 1.824 + 1.122x \quad &&\text{at 10 K.} \end{aligned} \tag{3}$$

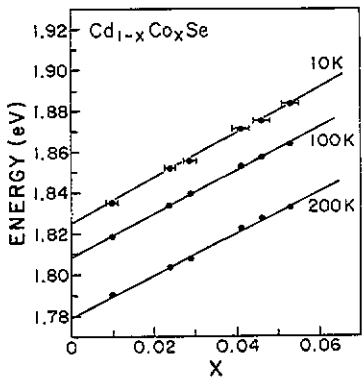

Figure 2. Energy E_0 in $Cd_{1-x}Co_xSe$ crystals as a function of composition, x, for three different temperatures. The solid lines are least-squares fits given by (3).

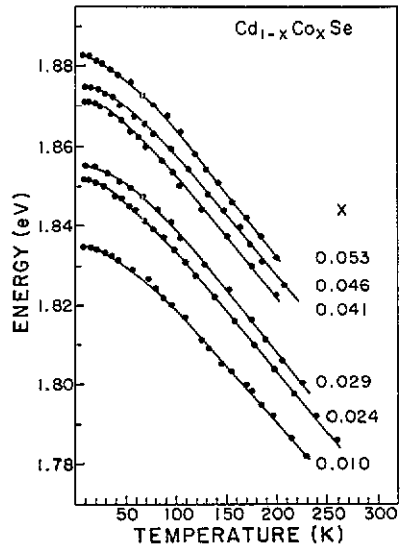

Figure 3. Energy of the A exciton as a function of temperature for various $Cd_{1-x}Co_xSe$ sample compositions. The solid lines are least-squares fits to the Varshni equation (4).

The results for dE_0/dx are smaller than the values found for $Cd_{1-x}Mn_xSe$ [10] and $Cd_{1-x}Fe_xSe$ [11]. However, the small span of the compositions studied does not allow us to draw any conclusions. The energy difference between the position of A and B excitons in the WMR spectra is about 25–26 meV in all the samples studied and does not vary with temperature or composition.

Table 1. Parameters obtained by fitting equation (4) to the E_0 against T data of figure 2.

Composition x	$E_0(0)$ (eV)	α (10^{-4} eV K^{-1})	β (K)
0.010±0.001	1.835	3.4	105
0.024±0.001	1.853	3.3	70
0.029±0.002	1.856	3.9	130
0.041±0.002	1.872	3.5	80
0.048±0.002	1.875	3.7	110
0.053±0.003	1.883	3.7	100

Figure 3 shows the energy variation of the A exciton with temperature for the $Cd_{1-x}Co_xSe$ system. Varshni [12] fitted the temperature variation of the energy gaps of many semiconductors to the following empirical formula

$$E_0(T) = E_0(0) - \alpha T^2/(\beta + T) \tag{4}$$

where β is proportional to the Debye temperature. An alternative phenomenological expression describing the variation of E_0 with temperature has recently been proposed [13]. It takes into account the renormalization of electronic states due to the interaction with phonons and has the form: $E_0(T) = E_B - a_B[1 + 2/(\exp(\theta/T) - 1)]$.

Here, θ is related to the average phonon frequency and a_B gives the strength of the interaction. We found that a better fit to the $E_0(T)$ data in $Cd_{1-x}Co_xSe$ alloys is obtained using Varshni's formula (3). The solid lines in figure 3 are least-square fits to (4). The parameters $E_0(0)$, α and β that were obtained for different compositions are given in table 1. The determined non-linear components do not vary significantly with composition. The relative errors of the α and β values are about 5% and 20%, respectively.

In conclusion, we have found that the energy gap of $Cd_{1-x}Co_xSe$ alloys varies linearly with composition in the range $0 < x \leqslant 0.053$. The temperature variation of the energy gap is fitted well by the empirical Varshni relation.

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