

Optical absorption of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ diluted magnetic semiconductors: Variation of the energy gap with composition and temperature

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(Received 4 January 2000; accepted for publication 8 November 2000)

Optical absorption and magnetic susceptibility data of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ family of compounds have been collected in the temperature range 10–300 K. One of the most interesting aspects of this series is the availability of samples in the whole composition range, in contrast with most diluted magnetic semiconductors that are only miscible in a limited range of compositions. Temperature-independent absorption bands with maxima at 2.33, 2.49, and 2.66 eV have been found that are assigned to electron transitions from the 6A_1 ground state to the 4T_1 , 4T_2 , and 4A_1 , or 4E excited states of the Mn^{++} ion in a tetrahedral crystalline field. The optical spectra exhibit a temperature dependent absorption edge in the 350–600 nm region that corresponds to a direct band gap. The band gap energy has been determined as a function of atomic concentration and temperature. At room temperature, the variation of the energy gap E_g with the Mn content shows a rather anomalous behavior that consists of an initial decrease for $x < 0.1$, followed by a roughly flat variation for $0.1 < x < 0.5$, and a nearly linear increase for $x > 0.5$. An analogous evolution of E_g with x is found when decreasing temperature. Such behavior has been compared with that reported for analogous systems. The variation of E_g with temperature follows Varshni's relation for all compositions. A monotonic increase of the magnetic susceptibility with x is found within the whole range of Mn content. © 2001 American Institute of Physics. [DOI: 10.1063/1.1337601]

I. INTRODUCTION

Diluted magnetic semiconductors (DMS) have attracted the attention of many scientists from various fields.¹ The scientific interest in these systems is based on their structural, electronic, optical, and magnetic properties.² They are also suitable for electro-optical applications and for the preparation of quantum wells and superlattices. The unique physical properties of diluted magnetic semiconductors arise from the interaction between localized magnetic moments of the magnetic ions and conduction and valence band electrons.

There are two distinct optical processes in Mn based DMS compounds. One of them is related to electron transitions between the valence band and the conduction band of the semiconductor. The other is related to internal electron transition in the Mn^{++} ions. Frequently, these two phenomena coincide within the same spectroscopic region and they are difficult to separate.³ They can be distinguished because they show a different variation with temperature and composition. The position of the energy maximum of intra-Mn transitions does not change with temperature and varies slightly with composition while the intrinsic transitions associated to a direct band gap change significantly with both temperature and composition.

One of the most interesting properties of DMS solid solutions for optical applications is the tunability of their band

gap with composition. Most work on optical properties of DMS solid solutions has been directed to $\text{A}_{1-x}^{\text{II}}\text{Mn}_x\text{B}^{\text{VI}}$ alloys.³ Usually, these compounds have a direct band gap that varies linearly with composition. In other words, they follow the virtual crystal approximation (VCA).¹ However, in some compounds, like $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ alloys,^{4,5} there is a deviation from linearity for low values of x . This deviation consists of the bowing of the E_g vs x plot for low Mn content. In these alloys, the parent compound $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ has wurtzite or zinc-blende crystal structure. In most cases, the structure of the parent compound is maintained in the alloy. However, substitution of the cation by Mn can be achieved over a limited range of x .¹

In this article we report optical absorption and magnetic susceptibility measurements in a less known type of DMS, the $\text{A}_{1-x}^{\text{II}}\text{Mn}_x\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ alloys. In particular, we have grown $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ single crystals in the range $0 \leq x \leq 1$. We have observed absorption bands in the optical absorption spectra of compounds with a high Mn content that are related to intra- Mn^{++} transitions. The variation of the band gap energy with the Mn content has been followed within the whole composition range. We have observed a non-VCA behavior that it is compared with that reported for other semiconductor alloys. The dependence of the energy gap on temperature has been determined for eight members of the series.

II. EXPERIMENT

Orange single crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($x=0.00, 0.10, 0.23, 0.49, 0.63, 0.75, 0.88, 1.00$) were prepared at our in-

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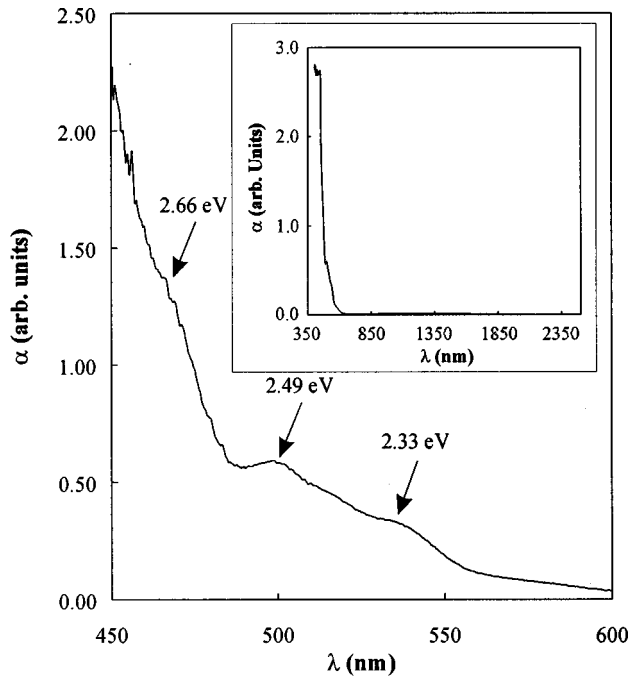


FIG. 1. Optical absorption spectra of MnGa_2Se_4 at 10 K, in the wavelength range from 450 to 600 nm, showing the maxima of the intra- Mn^{2+} absorption bands (black arrows). In the insert, idem, in the range from 350 to 2500 nm.

stitute, ICMA, by using the chemical vapor transport method following the growing conditions reported in the literature for the parent compounds,^{6–8} MnGa_2Se_4 and ZnGa_2Se_4 . Iodine was used as a transport agent. The purity of the samples was tested by means of conventional x-ray powder diffraction methods. No impurities were found. The Mn content of the samples was calculated from magnetic susceptibility data in the temperature region where the Curie–Weiss law applies. The Curie constant determined in this procedure is proportional to the amount of Mn^{2+} that is present in the sample. For additional details concerning this standard procedure, see, e.g., Ref. 9.

The crystals were polished with alumina powders to a thickness of less than 20 μm . Optical absorption measurements in the range 350–2500 nm were carried out in a Hitachi U-3400 spectrophotometer, from room temperature down to 10 K. As a reproducibility test, at least two different samples were measured for every composition. Magnetic measurements were performed in the same temperature region by using a superconducting quantum interference device magnetometer manufactured by Quantum Design.

III. RESULTS AND DISCUSSION

A. Mn intra-atomic transitions

No significant features were observed in the optical absorption spectra in the region from 600 to 2500 nm (insert in Fig. 1), apart from typical interference signals in samples with a thickness of a few microns.

The absorption spectrum of MnGa_2Se_4 at 10 K shows three bands with maxima at 532, 498, and 466 nm, respectively (Fig. 1). These absorption maxima are also present in

TABLE I. Intra- Mn^{2+} absorption maxima (in electrovolts) in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$, and in several DMS alloys with zinc-blende (z.b.) or wurtzite (w.) structure.

Compound	x	Transition			Source
		${}^6A_1 \rightarrow {}^4T_1$	${}^6A_1 \rightarrow {}^4T_2$	${}^6A_1 \rightarrow {}^4A_1, {}^4E$	
$\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$	1	2.33	2.49	2.66	a
	1		2.43		b
$\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ (z.b.)	0.001	2.34	2.48	2.66	c
	0.23	2.38	2.57	2.68	d
	0.5	2.42	2.54	2.70	d
					e
$\text{Cd}_{1-x}\text{Mn}_x\text{S}$ (w.)	0.4	2.43	2.58	2.72	e
$\text{Zn}_{1-x}\text{Mn}_x\text{S}$ (z.b. and w.)	0.007	2.22 ⁱ	2.44 ¹	2.63 ⁱ	f
	0.08	2.32	2.49	2.67	f
	0.5	2.38	2.52	2.68	g
$\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ (z.b.)	0.5	2.30	2.38	2.58	h
	0.6	2.33	2.44	2.61	h

^aThis work.

^bReference 13.

^cReference 33.

^dReference 3.

^eReference 4.

^fReference 14.

^gReference 34.

^hReference 35.

ⁱZero phonon lines.

the spectra of $x=0.88$ and $x=0.75$ samples. They are not observable at lower Mn content due to band broadening, and they are totally absent for $x=0$. These bands do not shift with temperature. Therefore, they are assigned to intra- Mn^{2+} transitions.

The coordination of the Mn^{2+} ion in the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series is expected to be tetrahedral since MnGa_2Se_4 and ZnGa_2Se_4 have been described in a defective chalcopyrite and defective stannite structure, respectively.^{10,11} The first excited state of Mn^{2+} , a d^5 configuration, is 4G . According to Sugano *et al.*,¹² the 4G state splits into 4T_1 , 4T_2 , 4A_1 , and 4E states in a tetrahedral crystalline field. Thus, the absorption bands observed at 2.33, 2.49, and 2.66 eV can be assigned to transitions from the 6A_1 ground state to the excited states 4T_1 , 4T_2 , 4A_1 , and 4E , respectively. In a previous study concerning the optical properties of MnGa_2Se_4 exclusively,¹³ Niftiev *et al.* found only one Mn band with a maximum at 2.43 eV that was associated with the ${}^6A_1 \rightarrow {}^4T_2$ transition.

Table I shows a comparison of Mn-related absorption bands seen in other DMS compounds with a Mn tetrahedral coordination, and the transitions they were assigned. Notice that the best agreement is obtained about the 2.66 eV band corresponding to the ${}^4A_1, {}^4E$ states, which are invariant with the strength of the crystalline field. On the other hand, Langer and Ibuki¹⁴ found a fine structure in Mn-bands that was interpreted in terms of phonon-coupled transitions. Therefore, real transition energies are given by zero-phonon lines and not by band maxima. Therefore, a determination of the crystalline field strength, Dq , and the Racah parameters, B and C ¹² for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ from our band maximum energies could only be approximate. On the other hand, the energies of band maxima we found and those reported in

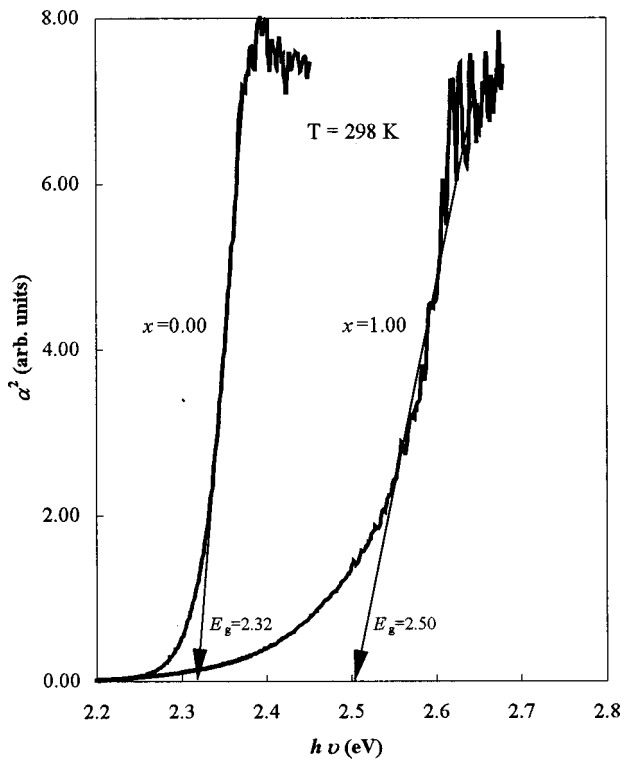


FIG. 2. Relation between the absorption coefficient squared α^2 and the photon energy $h\nu$ for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($x=0.00, 1.00$) at 298 K. The arrowhead lines are extrapolations of the straight portion of the plot to $\alpha^2=0$, which give the value of E_g .

Ref. 14 for $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ alloys are very similar. Therefore, the value of Dq in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ must be close to 480 cm^{-1} , which is the value calculated for $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ from the zero-phonon lines.

B. Energy gap

The plot of the absorption coefficient squared α^2 against the photon energy $h\nu$ yields a straight line near the fundamental absorption edge for all the samples, as it is shown in Fig. 2 for ZnGa_2Se_4 and MnGa_2Se_4 . This indicates a direct energy gap.¹⁵ We obtained a band gap energy E_g of 2.32 eV for ZnGa_2Se_4 at 298 K. This is among other values reported in the literature:¹⁶⁻¹⁸ 2.17, 2.18, and 2.465 eV. We find that $E_g=2.50$ eV for MnGa_2Se_4 at 298 K, which is also among previously reported values:¹⁹⁻²¹ 2.33, 2.56, 2.70, and 2.77.

The variation of the energy gap of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ solid solutions with composition is shown in Fig. 3. It is clear that, unlike most of $\text{A}_{1-x}\text{Mn}_x\text{B}^{\text{VI}}$ alloys,³ $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ does not follow the VCA.¹ With increasing Mn content, E_g first decreases to a minimum at $x\sim 0.1$, it is then roughly constant from $x\sim 0.1$ to $x\sim 0.50$, and it finally rises sharply beyond $x\sim 0.50$. A similar pattern is observed at low temperature except that the minimum deepens (Fig. 3).

Anomalous variations of the energy gap with composition for DMS alloys have been explained in many different ways in the literature. Bylsma *et al.*⁵ concluded that the minimum of E_g for low Mn content observed in $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ solid solutions^{5,22,23} is related to the variation of the magnetic susceptibility by the following equation:

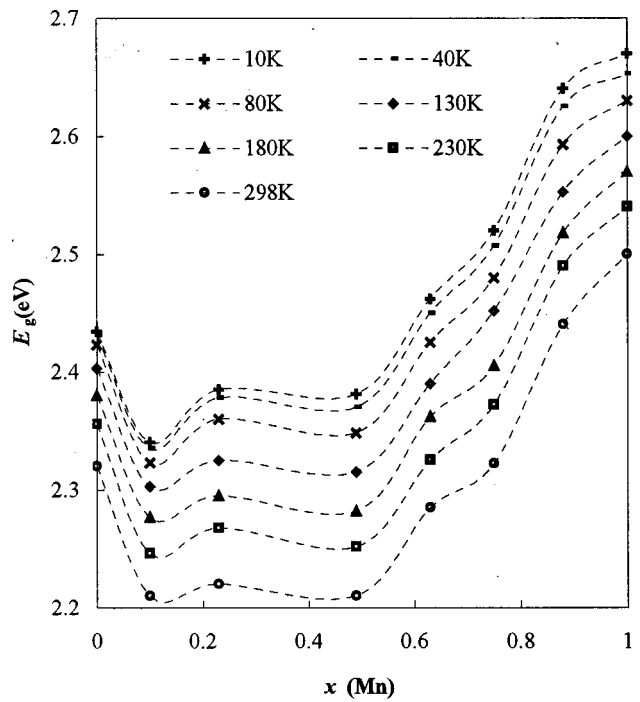


FIG. 3. Composition dependence of the optical energy gap E_g for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($x=0.00, 0.10, 0.23, 0.49, 0.63, 0.75, 0.88, 1.00$) at several temperatures. The lines are drawn to guide the eye.

$$E_g(x, T) = E_{0g}(x, T) - b\chi T, \tag{1}$$

where $E_{0g}(x, T)$ stands for the value of the energy gap when $\chi=0$, and b is a parameter that can be fitted. They derived Eq. (1) considering a coupling of band electrons and localized Mn spins, using a simple model based on second-order perturbation theory. Data points we have obtained for the susceptibility of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ are plotted versus x in Fig. 4. Clearly, nothing like the curves shown in Fig. 3 can be obtained from the data on Fig. 4, using Eq. (1) and a linear $E_{0g}(x)$ function. Consequently, the departure from VCA in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ cannot be explained in this way.

Indeed, the departure from VCA in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ may be unrelated to its semimagnetic character, because some nonmagnetic semiconductor alloys also exhibit behav-

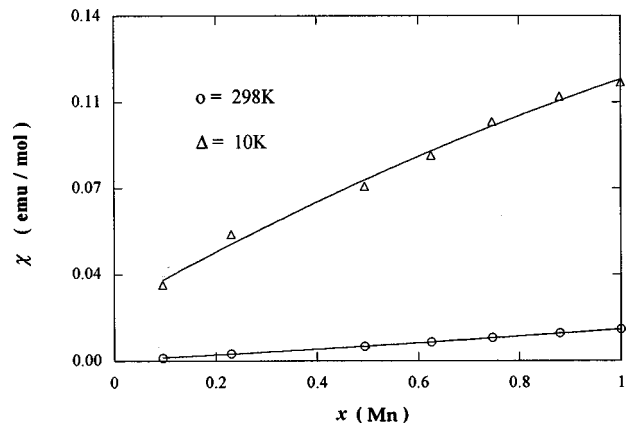


FIG. 4. Composition dependence of the magnetic susceptibility χ for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($x=0.00, 0.10, 0.23, 0.49, 0.63, 0.75, 0.88, 1.00$) at 10 and 298 K. The lines are drawn to guide the eye.

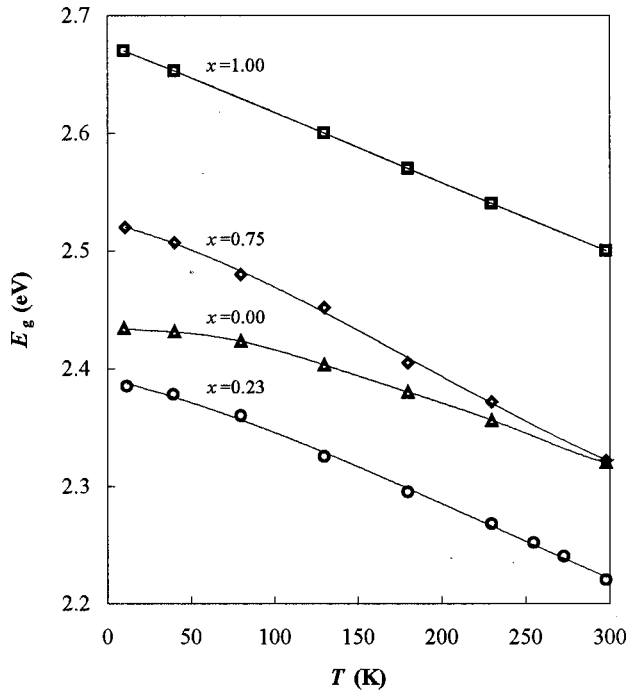


FIG. 5. Temperature dependence of the optical energy gap E_g for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($x=0.00, 0.23, 0.75, 1.00$). Solid lines show fits to the Varshni relation [$E_g(T) = E_g(0) - \alpha T^2/(T + \beta)$, where $E_g(0)$ represent the band gap energy at $T=0$ K, and α and β are constants of the material].

iors of this type.^{24,25} For the latter systems, several authors have found no relation between non-VCA behavior and changes in the crystal structure. For instance, E_g for ZnSe-ZnTe alloys²⁴ shows a nonmonotonic concave variation with x . Indeed, the variation of the lattice parameter with composition follows Vegard's law¹ throughout the whole range. Then, the anomalous variation of $E_g(x)$ was assigned to some unspecified property peculiar to Te atoms.²⁴ On the other hand, other diamagnetic solid solutions that do not contain Te, such as GaP-ZnS and GaP-ZnSe , also exhibit a non-VCA behavior.²⁵ Furthermore, the variation of the lattice constant with composition is linear for the GaP-ZnS and GaP-ZnS series that show a nonlinear variation of $E_g(x)$, whereas the lattice constant is nonlinear for the GaAs-ZnSe series that shows a linear variation of $E_g(x)$. Thus, the influence of structural factors on anomalous $E_g(x)$ variation, if any, is not clear.

Another attempt to explain non-VCA behavior has been made with regard to $\text{CdSnAs}_2\text{-In}_2\text{As}_3$, CdTe-AgInTe_2 , and CdTe-CuGaTe_2 alloys.^{26,27} The minimum in the $E_g(x)$ curves observed in these systems was related to the strong coulomb potentials that follows from the substitution of divalent ions (Cd and Sn) by trivalent ions (In and Ga).²⁸ Obviously, this explanation does not account for our results, since no valence change takes place upon ion substitution, even though Mn(II) is more ionic than Zn(II).

The variation of E_g with T for the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series is shown in Fig. 5. In the temperature range from 80 to 300 K, the energy gap decreases linearly for the whole series. The average temperature coefficient of the energy gap, dE_g/dT , calculated in this interval is given in Table II. Al-

TABLE II. Fitting of the E_g vs T dependence to the Varshni equation, and temperature coefficient values in the range from 80 to 300 K, for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$.

x	$-dE_g/dT$ ($\times 10^{-4}$ eV/k)	$E_g(0)$ (eV)	α ($\times 10^{-4}$ eV/k)	β (K)
0.00	4.7	2.435 (0.001)	6.9 (0.5)	233 (39)
0.10	5.3	2.341 (0.001)	7.0 (0.5)	172 (36)
0.24	6.2	2.391 (0.002)	6.9 (0.2)	68 (13)
0.49	6.3	2.383 (0.002)	8.5 (0.2)	32 (9)
0.75	7.4	2.522 (0.002)	7.9 (0.3)	49 (13)
0.88	6.9	2.648 (0.002)	7.0 (0.2)	0
1.00	6.0	2.674 (0.001)	6.0 (0.2)	0

though a regular trend cannot be deduced from the variation of dE_g/dT with x , the thermal shift of E_g appears to decrease with x in the low Mn content region. The temperature coefficient for MnGa_2Se_4 , -6.0×10^{-4} eV/K, is within values reported for MnGa_2S_4 , -7.5×10^{-4} eV/K,²⁹ and MnGa_2Te_4 , -5.0×10^{-4} eV/K.³⁰ On the other hand, the evolution of $E_g(T)$ for every composition fits well Varshni's relation³¹

$$E_g(T) = E_g(0) - \alpha T^2/(T + \beta), \quad (2)$$

where $E_g(0)$ represent the band gap energy at $T=0$ K, and α and β are constants of the material. Table II shows the values of the Varshni parameters obtained in the fitting. The decrease of β with the Mn content reflects a tendency of $E_g(T)$ to linearity. The addition of a susceptibility term to Eq. (2) as suggested by Bylisma *et al.*⁵ did not improve the fitting. This additional term was used to account for a coupling between band electrons and localized Mn spins. It can be inferred that this kind of magnetic effect is not of significant relevance in the $E_g(x, T)$ dependence exhibited by the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ compounds in the temperature range considered. However, it could be of interest to determine $E_g(x, T)$ at temperatures bellow 6.4 K that is the reported critical temperature for magnetic ordering in MnGa_2Se_4 .

IV. SUMMARY AND CONCLUSIONS

The optical absorption of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series has been measured for the whole composition range as a function of temperature. The spectra of compounds with a high Mn content show absorption bands corresponding to intra- Mn^{++} electronic transitions. These bands, with maxima at 2.33, 2.49, and 2.66 eV, have been assigned to internal Mn^{++} transitions from the 6A_1 ground state to the 4T_1 , 4T_2 , and 4A_1 or/and 4E excited states, in accordance with values reported for other Mn chalcogenides.

The variation of E_g with composition in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ solid solutions does not follow the virtual crystal approximation within the whole range of x . This anomalous variation of E_g with x has also been found in semiconductor alloys of very different kinds. The explanations proposed in the literature are vague and only apply to particular cases. This question remains open and should stimulate further research. Perhaps, the scheme of configuration interaction would throw some light onto the subject.³²

The evolution of E_g with temperature fits well Varshni relation. Such evolution presents a clear trend towards lin-

erarity with increasing Mn content. Due to magnetic ordering that MnGa_2Se_4 exhibits below 6.4 K, further experimental work below this temperature would be of interest. This would enable one to analyze the relevance of the magnetic effects on the energy gap as a function of composition and temperature.

ACKNOWLEDGMENTS

The authors are grateful to Dr. J. Fernández, Dr. J. Stankiewicz, Dr. R. Cases, Dr. V. Orera, and Dr. F. Palacio for their friendly assistance and comments. Financial support from CICYT (MAT97-951), DGA (Comunidad Trabajo Pirineos 97-98), and CAI+DGA (Programa Europa) is also acknowledged.

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