Order-disorder phase transition in $Zn_{1-x}Mn_xGa_2Se_4$: Long-range order parameter versus x

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The opportunity of the $Zn_{1-x}Mn_xGa_2Se_4$ $(0 \leqslant x \leqslant 1)$ series for exploring the possibilities of ordering-disordering processes as a function of x is shown. A pumping of Mn ions from one particular site of the crystal lattice to another occurs in this system on addition of Zn. As a consequence, the tetragonal diluted magnetic semiconductor $Zn_{1-x}Mn_xGa_2Se_4$ series exhibits an order-disorder phase transition at $x_c = 0.50 \pm .01$ with $(c/a)_c = 1.964 \pm .005$. The disordering process is accompanied by an abrupt change in the tetragonal unit cell parameters c and 2-(c/a), a modification of the crystal lattice from defective chalcopyrite to defective stannite and a crossover from space group I-4 to I-42 m. The order-disorder phase transition has been quantified through the direct determination of a long-range order parameter η within its whole range of existence $(0 \leqslant \eta \leqslant 1)$.

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I. INTRODUCTION

Spontaneous ordering on atomic scales in alloys has attracted increasing interest in connection with theoretical studies[1,2] and current efforts in the development of high-performance systems for novel device applications.[3] Deviations from the atomically disordered state may strongly alter the electronic band structure of a semiconductor alloy, with resulting changes in its electrical and optical properties.[4,5] Therefore, the possibility of tuning those properties via control of the degree of cation ordering has a particular significance.[6] A quantitative determination of the degree of ordering is therefore extremely valuable. The degree of order-disorder can be quantified through the use of long range order parameters ranging from 0 to 1 for, respectively, total cation disorder and perfect alloy ordering. Optical properties are often used to estimate the degree of order in semiconductor alloys through the application of theoretical calculations.[7] So far, experimental determination of the degree of cation ordering and direct measurements of long-range order parameters have been lacking. Moreover, an atomistic understanding of the ordered alloy formation mechanism is far from clear.

Cation ordering has been observed in epitaxially grown pseudobinary III-V and II-VI semiconductor alloys.[8,9] Surprisingly, these atomically ordered structures have no counterpart in the phase diagram of the bulk form at the same composition and temperature ranges.[10] The degree of ordering within the metastable layers depends on parameters strongly dependent on surface effects that can be understood from fundamentals of strain and surface reconstruction.[11,12] As a consequence of experimental attempts to obtain new semiconductor series, some order-disorder phenomena have been described to occur in II-III-VI_2 chalcopyrites with increasing temperature.[13,14] The related defective family II-III_2-VI_4, which is characterized by an ordered sublattice of vacancies and then by a further degree of freedom as to tailoring possibilities, has on the other hand received much less attention probably due to its higher degree of complexity.[15]

In a different approach, the partial substitution of non-magnetic constituents of a semiconductor compound by magnetic ions produces a diluted magnetic semiconductor (DMS) with magnetic properties which distinguish them from ordinary semiconductors. The interaction between the localized magnetic moments of the magnetic ions and the conduction and/or valence band electrons results in an unusual combination of optical, magnetic, and electronic properties that make DMS's interesting subjects for scientific and applied investigation.[16,17] Those properties can be tuned, by tailoring the composition through the use of solid solutions, to precisely match specific requirements.[18,19] However, one of the problems encountered in most of bulk DMS's is the absence of complete solid solubility which restrict the experimental access to certain ranges of x values.

The exploration of further possibilities for ordering-disordering processes in semiconductors has motivated this work. Although much information has been reported concerning order-disorder transitions in epilayers of pseudobinary semiconductors and its influence on the optoelectronic properties, no such studies have been reported for DMS's. However, interesting results are expected in these systems by relating cation ordering to the optical, electronic, and magnetic properties. In this work we analyze the degree of ordering of magnetic ions in a DMS series. For this purpose we have chosen the series $Zn_{1-x}Mn_xGa_2Se_4$ $(0 \leqslant x \leqslant 1)$ which can be synthesized in the whole range of composition x.

II. EXPERIMENT

Orange single crystals of $Zn_{1-x}Mn_xGa_2Se_4$ with $x = 0.00$, 0.104(4), 0.240(4), 0.343(4), 0.482(4), 0.63(1), 0.77(1), 0.900(7), and 1.00 were prepared using the chemical vapor transport method[20,21] at the Instituto de Ciencia de Materiales de Aragón.

Time-of-flight neutron powder diffraction data were collected on the Polaris diffractometer[22] at the ISIS source, Rutherford Appleton Laboratory, UK. The samples were encapsulated inside thin-walled vanadium cans. Diffraction data were collected at room temperature in all available detector

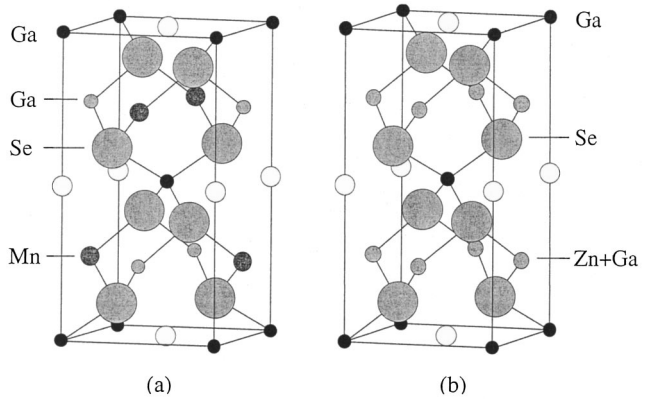

FIG. 1. Tetragonal unit cells of $MnGa_2Se_4$ (a) and $ZnGa_2Se_4$ (b), space groups I-4 and I-42m, respectively. The coordinates of relevant sites are 2(a): (0,0,0); 2(b): $(0,0,\frac{1}{2})$; 2(c): $(0,\frac{1}{2},\frac{1}{4})$; 2(d): $(0,\frac{1}{2},\frac{3}{4})$; 4(d): $(0,\frac{1}{2},\frac{1}{4})$, and $(0,\frac{1}{2},\frac{3}{4})$.

banks over a d-spacing range $0.5<d(\text{Å})<12.0$, although refinements reported here were carried out in the range $0.8<d(\text{Å})<3.2$ using the highest-resolution backscattering detectors with an essentially constant resolution of $\Delta d/d\sim 5\times 10^{-3}$. Preliminary data reduction, including normalization and correction for sample absorption, was carried out using GENIE spectrum manipulation software.[23] The analysis of the diffraction patterns was performed by Rietveld refinements using the program TF14LS (Ref. 24) which is based on the Cambridge Crystallographic Subroutine Library.[25] The total Mn concentration x of each of the members of the series has been obtained from the refinements as the sum of the Mn site occupancy factors. No significant difference can be observed between the actual and the nominal value of such concentration (quantity of Mn used on the synthesis).

III. RESULTS AND DISCUSSION

The defective chalcopyrite $MnGa_2Se_4$, space group I-4 with $a=5.677(1)$ Å and $c=10.761(2)$ Å, shows a completely ordered cation distribution [see Fig. 1(a)].[26] However $ZnGa_2Se_4$ possesses a partial disordering of the cations with $a=5.5117(3)$ Å and $c=10.9643(6)$ Å and a defective stannite structure, space group I-42 m [see Fig. 1(b)].[27] The difference in the cation distribution is that in $MnGa_2Se_4$ the Mn atoms and half of the Ga atoms are placed in different lattice positions 2(d) and 2(c), respectively, while in $ZnGa_2Se_4$ the Zn and half of the Ga atoms share the same lattice site 4(d). In fact, the positions associated with 2(d) plus those corresponding to 2(c) in I-4 are equivalent to those associated with 4(d) in I-42 m (see Fig. 1). The remaining gallium atom of the unit formula occupies the same lattice position 2(a) in both $MnGa_2Se_4$ and $ZnGa_2Se_4$, as do the vacancies located at the 2(b) site. Could a progressive and controlled substitution of Mn by Zn in the $MnGa_2Se_4$ lattice induce a crossover from an ordered to a disordered Mn cation distribution? In the case of an affirmative response the process could be followed step by step since the series can be synthesized within the whole range of composition $0\leqslant x\leqslant 1$.

The evolution of the tetragonal unit cell parameters of the $Zn_{1-x}Mn_xGa_2Se_4$ series, calculated from the powder diffraction data, is presented in Fig. 2 as a function of the manganese content. The unit cell volume presents a linear dependence on the x parameter (Fig. 3) which can be very useful for a determination of the concentration of manganese in other synthesized members of the series. Although the evolution of the unit cell parameter a with x is nearly linear, the c parameter is affected by an abrupt change of slope at $x=0.49\pm 0.01$ (Fig. 2). For lower manganese concentrations the unit cell parameter c does not vary with x while for higher values it decreases rapidly until the end $x=1$ is reached. Thus, a significant change is suggested to occur in the series at intermediate values of dilution. Moreover, the representation of the deviation from the cubic symmetry $2-(c/a)$ versus x also shows a clear variation of slope at $x=0.50\pm 0.01$ (see Fig. 3). What can be the origin of such a change in the unit cell dimensions at intermediate values of the degree of dilution?

Since the space group which best describes the crystal structure of $ZnGa_2Se_4$ is I-42 m and that of $MnGa_2Se_4$ is I-4, a crossover from I-4 to I-42 m is expected to occur within the $Zn_{1-x}Mn_xGa_2Se_4$ series as the content of zinc is

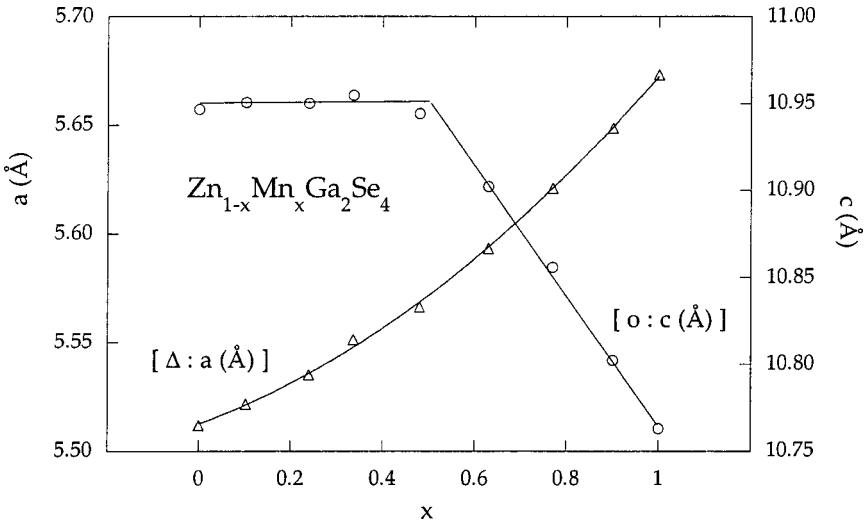

FIG. 2. Dependence of the tetragonal unit cell parameters of $Zn_{1-x}Mn_xGa_2Se_4$ ($0\leqslant x\leqslant 1$) on the Mn content. The solid lines are an eye guide and the error bars of the data are $\leqslant$ the size of the symbols (as in the rest of figures, if no additional specifications are given).

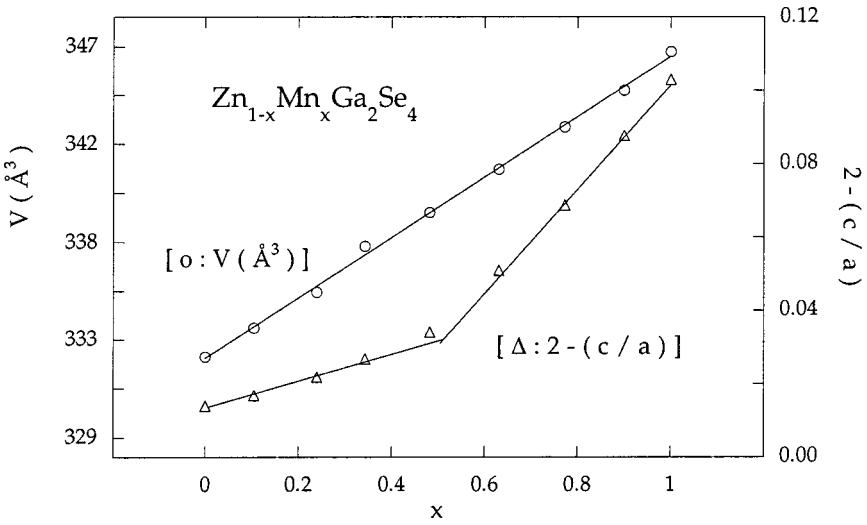

FIG. 3. Unit cell volume and axial ratio $2\text{-}c/a$ of tetragonal $Zn_{1-x}Mn_xGa_2Se_4$ $(0 \leqslant x \leqslant 1)$ in terms of x.

gradually increased. Reflection conditions are the same for both space groups. Thus, the relevant criteria for choosing between $I\text{-}4$ and $I\text{-}42$ m are the values of the X and Y positional coordinates of the Se atom. These two coordinates are equal in $I\text{-}42$ m, for symmetry reasons, but can take different values in the case of $I\text{-}4$. The dependence of the Se coordinates on x, calculated from full Rietveld structure refinements, is shown in Fig. 4. As a result, $I\text{-}4$ is found to be the space group which best describes the crystal symmetry of $x = 1.00$, 0.90, 0.77, and 0.63 while $I\text{-}42$ m is found to be the best choice for $x = 0.48$, 0.34, 0.24, 0.10, and 0.00. Therefore a crossover between $I\text{-}4$ and $I\text{-}42$ m symmetries takes place at intermediate values of the degree of Mn-Zn dilution. This coincides with the changes that the unit cell parameters c and $2\text{-}(c/a)$ exhibit within that x range.

A. Order-disorder phase transition

Gastaldi *et al.*[28] proposed a relationship between the axial ratio c/a and the cation ordering in the II-Ga_2-VI_4 series (II=Co,Cd,Hg; VI=S,Se,Te). As a consequence, since c/a is significantly smaller than 2 in the case of $MnGa_2Se_4$ $(c/a = 1.90)$, a complete ordering of cations should be expected for this compound as it is experimentally found. However, the value of c/a is nearly 2 for $ZnGa_2Se_4$ $(c/a = 1.99)$. Following Gastaldi *et al.*, a partial ordering of cations can be predicted for the crystal structure of this compound. The decrease of c/a versus x within the $Zn_{1-x}Mn_xGa_2Se_4$ series (Fig. 5) would then suggest a tendency to an increase of cation ordering when going from $x = 0$ to $x = 1$.

The distribution of the Mn cations in the lattice as a function of x is calculated from Rietveld refinements of the powder diffraction patterns and is shown in Fig. 6. Due to the negative coherent nuclear scattering length of manganese, this element is clearly detected by the neutron diffraction technique. All the Mn atoms in $MnGa_2Se_4$ are located at a well defined lattice position $2(d)$ exhibiting a completely ordered scheme. A pumping of magnetic ions from $2(d)$ to an inequivalent lattice site $2(c)$ starts as the x parameter decreases, raising the $x^{(c)}/x^{(d)}$ ratio, where $x^{(c)}$ and $x^{(d)}$ represent the proportion of manganese in, respectively, $2(c)$ and $2(d)$ sites. The probabilities of a Mn ion occupying the $2(d)$ and $2(c)$ sites become equal at intermediate values of x and the two sites come to be crystallographically equivalent

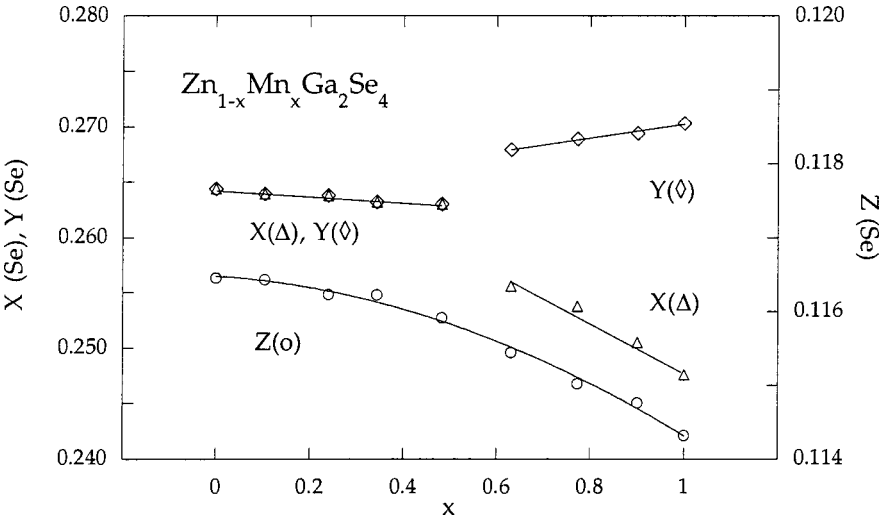

FIG. 4. Evolution of the Selenium coordinates X, Y, and Z, with the Mn content in $Zn_{1-x}Mn_xGa_2Se_4$ $(0 \leqslant x \leqslant 1)$.

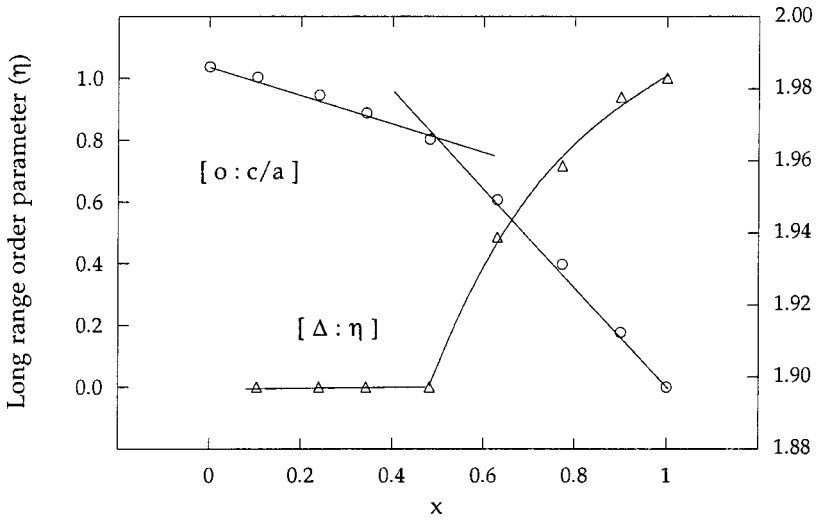

FIG. 5. Long-range order parameter $\eta = [x^{(d)} - x^{(c)}]\,[x^{(d)} + x^{(c)}]$ and axial ratio (c/a) as a function of x in $Zn_{1-x}Mn_xGa_2Se_4$ $(0 \leqslant x \leqslant 1)$. The variables $x^{(d)}$ and $x^{(c)}$ represent the Mn site occupancy factor of, respectively, 2(d) and 2(c) sites in I-4 and 4(d) in I-42m for which $x^{(d)} = x^{(c)}$.

[4(d) site in space group I-42m]. This situation is retained as x decreases down to $x = 0$.

Therefore an order-disorder phase transition, involving the magnetic ions, occurs within the $Zn_{1-x}Mn_xGa_2Se_4$ series as function of the manganese content. A critical point $x_c = 0.50 \pm 0.01$ can be calculated from the evolution of the Mn cation distribution with x shown in Fig. 6, in good agreement with the value obtained from the changes of the unit cell dimensions (Figs. 2 and 3) and the crossover between I-4 and I-42m space groups (Fig. 4). For any given x value the corresponding manganese distribution can be straightforward deduced from Fig. 6. It is remarkable the simplicity and beauty of the $Zn_{1-x}Mn_xGa_2Se_4$ series with respect to the distribution of the magnetic cations on the lattice sites as a function of x. In particular, it is interesting to note that the critical point is located at precisely the intermediate value of the x parameter.

The order-disorder processes occurring in defective II-III_2-VI_4 semiconductors have been predicted to take place in two stages as the temperature is increased.[29] In the first stage, the cations mutually substitute for one another. In the second, a cation-vacancy disorder occurs. Interestingly, the x dependent order-disorder phase transition exhibited by the $Zn_{1-x}Mn_xGa_2Se_4$ series can be assigned to that first stage of disorder. On the other hand, the I-III-VI_2 and II-IV-V_2 ternary families of chalcopyrites exhibit an order-disorder phase transition as a function of temperature from the chalcopyrite room temperature phase to a disordered zinc blende structure.[30] This transition has been shown to take place for those chalcopyrites exhibiting a room temperature axial ratio $(c/a) > 1.95 \pm .01$. Compounds with room temperature unit cell parameters $(c/a) < 1.95$ remain in the chalcopyrite structure up to the melting point.

Remarkably, a critical value of $(c/a)_c = 1.964 \pm 0.005$ can be deduced from Figs. 3 and 5 associated with the critical concentration $x_c = 0.50 \pm .01$ at which the order-disorder phase transition occurs in the $Zn_{1-x}Mn_xGa_2Se_4$ series. Interestingly, both critical values of the axial ratio c/a 1.964 ± 0.005 and 1.95 ± 0.01, coincide within the experimental error. A remarkable parallelism between the effects of the concentration and the temperature variables on the degree of disorder in chalcopyrites is suggested. The dilution of Mn with Zn could be regarded as the agent responsible for the increase of the entropy associated with the disordering pro-

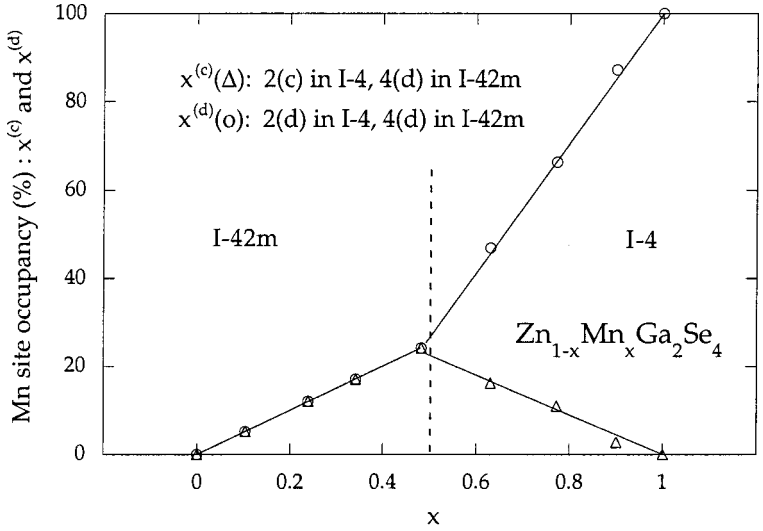

FIG. 6. Distribution of the Mn ions in the diluted magnetic semiconductor $Zn_{1-x}Mn_xGa_2Se_4$ $(0 \leqslant x \leqslant 1)$ series as a function of the concentration of the magnetic ion. There is a change of space group at intermediate values of x, from I-4 $(0.50 < x \leqslant 1)$ to I-42m $(0 \leqslant x < 0.5)$, as the magnetic dilution increases.

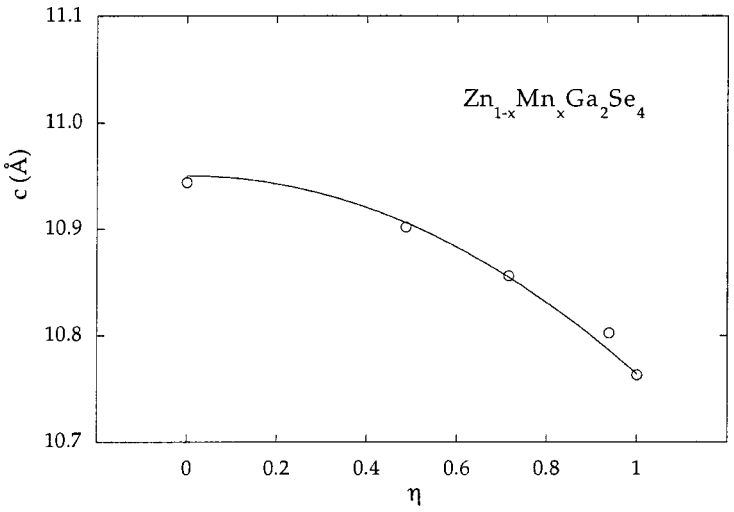

FIG. 7. Experimental (o) and calculated (line) values of the c axis for the $Zn_{1-x}Mn_xGa_2Se_4$, series, in terms of the long-range order parameter η (see text for details).

cess in the $Zn_{1-x}Mn_xGa_2Se_4$ series. In parallel, the increase of temperature can be considered as the agent responsible for the increase of the entropy associated with the disordering process in chalcopyrites. The dilution of Mn with Zn in $Zn_{1-x}Mn_xGa_2Se_4$ could be comparable to the increase of the temperature in chalcopyrites in the sense that both produce an increase of the degree of cation disorder.

B. Long-range order parameter

The order-disorder phase transition that the $Zn_{1-x}Mn_xGa_2Se_4$ series exhibits is expected to be of second order due to the gradual change in symmetry with x. Moreover I-4 is a subgroup of I-42m. In order to quantify the nature of the phase transition, we have defined a long-range order parameter $\eta=[x^{(d)}-x^{(c)}]/[x^{(d)}+x^{(c)}]$. In this expression, $x^{(c)}$ and $x^{(d)}$ represent the proportion of manganese in, respectively, $2(c)$ and $2(d)$ lattice sites for space group I-4 [$4(d)$ for I-42m]. Any observable quantity which varies with temperature, pressure, or any other independent variable can be taken as an experimental order parameter. In fact, the above definition of η is inspired by the mathematical expression of the long-range order parameter ξ described for typical alloys exhibiting order-disorder phase transitions as a function of the temperature.[2] In this role $\xi=(R-W)/(R+W)$ where R denotes the fraction of ''right'' atoms ($x^{(d)}$ in our case), W the number of ''wrong'' atoms ($x^{(c)}$ in our case) and $R+W$ gives the total fraction of atoms of a particular kind. The fraction of Mn atoms $x^{(d)}$ and $x^{(c)}$ have been obtained from the determination of the corresponding lattice site occupancy factors (see Sec. III A). The variables R and W change with temperature. However, in the series under study the relevant variable is the composition of the system and thus $x^{(d)}$ and $x^{(c)}$ change with x at room temperature. The highest order of the alloy corresponds to $x^{(d)}=1$, that is $x^{(c)}=0$, and $\eta=1$ is the value of the order parameter for this state. In the completely disordered state, $x^{(d)}=x^{(c)}$ and the order parameter associated with this state is $\eta=0$.

The evolution of η with the manganese content is shown in Fig. 5. The long-range order parameter we have defined for the series under study decreases continuously from $x=1$ to $x=0.5$ since the disorder of the system increases simultaneously. For $x<0.5$ the order parameter η is zero since the disorder of the Mn cations in the available lattice site is complete. Therefore the degree of ordering of the magnetic cations in the DMS $Zn_{1-x}Mn_xGa_2Se_4$ can be tuned from total order to total disorder by tailoring the composition of the system. This is interesting because the optical and electronic properties of semiconductors have been established to depend on the long-range order parameter.[4,5] On the other hand, recent studies in semiconductor epilayers have shown the dependence on substrate orientation of the critical point associated with order-disorder phenomena.[31] In that case, the corresponding order parameter must be linked to a particular lattice direction. The long-range order parameter determined for $Zn_{1-x}Mn_xGa_2Se_4$ is three dimensional in character in the sense that it takes into account all the directions of the lattice and not only a particular one.

In order to describe the properties of partially ordered alloys as a function of the degree of ordering, a general relation based on a statistical description of substitutional $A_{1-x}B_x$ system was deduced by Laks *et al.*[32,5] in terms of the Ising model. Thus, the expression $P(\eta)=P(0)+\eta^2[P(1)-P(0)]+O(\eta^4)$ relates an invariant under atomic interchange lattice property $P(\eta)$ of a partially ordered alloy with $P(\eta=0)$ and $P(\eta=1)$, the properties of the fully disordered and perfectly ordered cases, respectively. If $P(\eta)$ is antisymmetric with respect to interchange of A and B then η^2 must be replaced by η in the above expression. The correction $O(\eta^4)$ is due to four-body and higher interactions which are much weaker than the pair interactions. The expression of Laks *et al.* has been tested, within a limited η range, to hold for optical data.[33] We have applied this equation to the unit cell parameter of the series which is neatly affected by the order-disorder process. Thus, the agreement between experimental and calculated data are shown in Fig. 7 for the c axis. This figure illustrates the validity of the approximation to predict the long-range order parameter of an alloy from the experimentally determined unit cell parameters. As already mentioned, a quantitative determination of the degree of ordering in semiconductor alloys is particularly valuable. Significantly, the $Zn_{1-x}Mn_xGa_2Se_4$ series provides a test of

the model by Laks *et al.* over the whole range of existence of the long-range order parameter η. Previous analysis of the accuracy of that approximation comparing with experimental $P(\eta)$ data involved only small η ranges.[33] Moreover, the equation requires knowledge of $P(1)$ and $P(0)$ which are not always attainable experimentally.[5] These two magnitudes, associated to the fully ordered and disordered cases, are available in the $Zn_{1-x}Mn_xGa_2Se_4$ series since both states, corresponding to $\eta=1$ and $\eta=0$, can be obtained in the laboratory. This fact open the field for additional experiments and should stimulate further research. The fingerprint of the degree of dilution of the Mn cations in the magnetic properties of this series will be reported in a separate paper.

IV. CONCLUSIONS

The opportunity of the $Zn_{1-x}Mn_xGa_2Se_4$ $(0\leqslant x\leqslant 1)$ series for exploring the possibilities of ordering-disordering processes as a function of x is shown. A pumping of magnetic ions occurs in this family of compounds from one particular site within the crystal lattice to another as soon as the dilution process with Zn starts. As a consequence, the series exhibits an order-disorder phase transition at $x_c=0.50\pm0.01$. The disordering process is accompanied by an abrupt change in the tetragonal unit cell parameters c and $2-(c/a)$, a crossover from space group $I\text{-}4$ to $I\text{-}42m$ and a modification of the crystal structure from defective chalcopyrite to defective stannite.

A critical value for the axial ratio $(c/a)_c=1.964\pm0.005$ has been also determined. Above this point the magnetic cations are distributed at random while for lower c/a values they present a partial or even total ordering. This critical point coincides, within the experimental error, with the axial ratio $c/a=1.95\pm0.01$ found for chalcopyrites of the type I-III-VI_2 and II-IV-V_2. Interestingly, the order-disorder phase transition reported for these two last families takes place as a function of the temperature while in the case of the $Zn_{1-x}Mn_xGa_2Se_4$ $(0\leqslant x\leqslant 1)$ series the transition is driven by the composition of the system.

The order-disorder phase transition, described for $Zn_{1-x}Mn_xGa_2Se_4$, has been quantified through the experimental determination of a three-dimensional long-range order parameter η within its whole range of existence $(0\leqslant\eta\leqslant 1)$. Thus, the degree of ordering of the magnetic cations can be tuned from its minimum $(\eta=0)$ to its maximum value $(\eta=1)$ by tailoring the composition. The series also illustrates a simple procedure to calculate the degree of ordering and the long-range order parameter of an alloy from the easily measured unit cell parameters. This is particularly useful due to the strong dependence of the optoelectronic properties of semiconductors on η.

The $Zn_{1-x}Mn_xGa_2Se_4$ $(0\leqslant x\leqslant 1)$ series can be considered as a unique DMS system in the sense that it provides, as a function of $0\leqslant x\leqslant 1$, a clear demonstration of the occurrence of an order-disorder phase transition in a DMS, a quantitative characterization of the distribution of the magnetic ions, and a direct determination of the corresponding long-range order parameter. We hope that our work will stimulate extended investigation on the degree of cation ordering in DMS's and its fingerprint in the optical, electronic, and magnetic properties of these interesting materials.

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