Order/disorder phenomena in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ordered vacancy compounds: high temperature neutron powder diffraction experiments

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Abstract

We present a study of order-disorder phenomena in the series of tetrahedral ordered vacancy compounds $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ by means of time-of-flight neutron diffraction at high temperature together with dc magnetic susceptibility, Raman spectroscopy, differential thermal analysis and optical absorption experiments. Samples of nominal composition $x = 0, 0.24, 0.5, 0.77$ and 1 have been studied. An order-disorder phase transition has been detected, with T_c ranging from 472 to 610 °C, which involves a structural change from a defect chalcopyrite phase, with $I-4$ space group (s.g.) and three different cation sites, to a partially disordered defect stannite, in which Zn, Mn and half of the Ga ions share the 4d site in $I-42m$ s.g. Neither the vacancies nor the Ga ions occupying site 2a are involved in the phase transition. An additional *ordering* process is observed on approaching the phase transition from below, which is attributed to several factors: the activation of cation diffusion at ~ 300 °C, the partially disordered cation distribution exhibited by the as-grown single crystals and the preference of Mn atoms for the 2d crystallographic site in the $I-4$ structure. The reversibility of the phase transition is analyzed with the aid of magnetic, optical and Raman experiments.

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1. Introduction

$\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0 \leq x \leq 1$) compounds belong to the family of $\text{A(II)B(III)}_2\text{X(VI)}_4$ ordered vacancy compounds (OVC) [1,2]. They present a unique combination of properties such as non-centrosymmetry, optical anisotropy and high optical non-linearity, which make them interesting and promising materials for optical, electronic, and optoelectronic applications [2-5].

The presence of three different cations allows a rich variety of order/disorder phenomena to occur, depending on how the cations are distributed amongst the available sites. Order/disorder phenomena, and specifically those related to cation distribution, are known to affect the physical properties of semiconductors and their possible applications. For instance, cation disorder may introduce additional states in the gap, resulting in the lowering of the gap energy [6]. The lattice parameters and unit cell volume may also vary as a function of cation distribution [7]. In magnetic compounds a disordered cation distribution also results in dramatic changes in the magnetic properties [8].

As regards the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series, electronic band gap and magnetic properties have been shown to vary non-monotonically with composition [9-11], a fact that has been attributed to a varying degree of disorder along the series. This hypothesis has been verified in a structural study performed by means of time of flight (TOF) neutron diffraction at room temperature (RT) [10-13]. As reported in [10], the degree of order is closely related to the Mn occupancy of the available sites: 2d and 2c (if the space group is $I-4$) or 4d (if it is $I-42m$). The end compound MnGa_2Se_4 crystallizes in a fully ordered defect chalcopyrite (DC) structure with $I-4$ space group (s.g.). For this compound, each crystallographic site is occupied by a single type of cation: 2d site by Mn and 2a and 2c sites by Ga. As the Mn concentration decreases, Mn occupancy in the 2c site is increased, giving rise to partial

structural disorder. For $x = 0.5$ and below, Zn, Mn and half of the Ga cations share a common site and the structure transforms to defect stannite (DS) with $I-42m$ s.g. An order parameter was defined in [10] as $\eta = (x_d - x_c)/(x_d + x_c)$, where x_d and x_c represent the Mn occupancy of 2d and 2c sites in $I-4$ s.g., respectively. Full order ($\eta=1$) occurs if Mn exclusively occupies the 2d site, whereas full disorder ($\eta=0$) occurs if $x_d = x_c$, in which case the structure changes to DS. Intermediate situations occur, in which the s.g. is still $I-4$ but Mn partially occupies the 2d and 2c sites, resulting in $0 < \eta < 1$. As regards the anions, the Se location changes from the general site 8g with (x,y,z) coordinates in $I-4$ s.g. to the 8i site (x,x,z) in $I-42m$ s.g., so that the difference $x(\text{Se}) - y(\text{Se})$ is also an indicator of the degree of order. Finally, the tetragonal distortion parameter $\sigma = 2 - c/a$ can also be used to measure the degree of disorder: σ is close to 0 for compounds with the DS structure ($c \sim 2a$) and increases with increasing order of the cation distribution in DC compounds ($c < 2a$).

Thermally induced order/disorder phenomena are well known in chalcopyrite-like ABX_2 semiconductors, some of which undergo a phase transition to a zincblende phase, with a fully disordered cation distribution, at temperatures in the range of 900-1200 K [14,15]. Reports of phase transitions in DC or DS compounds are less common, and most of them are based on high pressure experiments [16-24], in which different stages of cation disorder are observed.

As regards the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series, previous reports on high temperature anomalies detected by differential thermal analysis (DTA) and attributed to phase transitions can be found in [25]. However, neither the nature of the anomaly nor the precise symmetry of the intervening phases were supported by crystallographic data in that work.

Our own DTA data (see section 3) show the existence of a thermal anomaly with a transition temperature (T_c) between 470 and 610 °C, depending on composition. The change

of the s.g. at RT as a function of composition around $x=0.5$ [11], as well as the detection of changes in the degree of order as a function of thermal treatments by other techniques, mainly by Raman spectroscopy [26,27], suggest that the DTA thermal anomaly might be due to a phase transition of the order/disorder type. In order to verify this hypothesis and, more generally, to study order-disorder processes in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ compounds, a high temperature structural analysis has been performed by means of neutron diffraction experiments.

To investigate the changes undergone by the sample upon the heating-cooling cycle, complementary magnetic (main text), optical (supplementary material) and Raman experiments (previous results and supplementary material) were performed.

2. Experimental details

Orange-coloured single crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($x=0, 0.24, 0.50, 0.77$ and 1) were synthesized by the Chemical Vapour Transport (CVT) method [28,29], with the aim of obtaining a series of materials presenting interesting structural, magnetic and optical phenomena. That technique was chosen because it is known to provide a high degree of chemical purity. Stoichiometric quantities of Mn, Zn, Ga and Se were placed in a 20 cm long quartz ampoule that was evacuated at a pressure better than 10^{-6} mmHg in order to prevent oxidation of the samples. A suitable amount of iodine was added by distillation (4 mg/cm^3). After that procedure the ampoule was sealed and placed horizontally in a two-zone furnace. The temperature of the ampoule was gradually increased along one week from room temperature up to 850°C for the source zone (one end of the ampoule) and 900°C for the deposition zone (the other end). After that, the temperature of both zones was reversed (850°C for the deposition zone and 900°C for the source zone). This gradient of

temperature was maintained for one week. To finish, the ampoule was removed from the furnace at high temperature and the source zone was cooled under tap water in order to prevent the precipitation of gaseous phases over the crystals already grown on the deposition zone.

Time-of-flight (TOF) neutron powder diffraction experiments were performed at the Polaris diffractometer at the ISIS source in the Rutherford Appleton Laboratory (UK). Powdered samples were heated in an open vanadium can up to $\sim 650^\circ\text{C}$, under a vacuum of 9×10^{-4} mmHg in order to prevent oxidation of the samples.

Differential Thermal Analysis (DTA) was performed on these materials using a TA Instruments STD 2960 equipment. Powdered samples were heated at a rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow.

DC magnetic susceptibility data were collected as a function of the temperature in a magnetometer manufactured by Quantum Design with superconducting quantum interference device detection. The experiment was performed under an external magnetic field of 1 T on polycrystalline samples before and after the thermal treatment associated to the neutron diffraction experiments.

Raman measurements were recorded using a DILOR XY spectrometer with a liquid nitrogen cooled CCD detector and excitation at 514.5 nm through a X50 microscope objective lens. Optical absorption curves were obtained from diffuse reflectance measurements performed in a Varian 500 spectrophotometer.

3. Experimental results

3.1. DTA experiments

Table 1 shows the temperatures of the thermal anomalies found by DTA. They vary smoothly between 470 and 610 °C, depending on composition. Contrary to the results of [25], no discontinuity is found at any Mn concentration.

3.2. Neutron diffraction

Three diffraction patterns were collected for each sample: one at room temperature (RT) and two at high temperature but close to the phase transition: one (T_1) below T_c and the other one (T_2) above T_c . Note that T_1 and T_2 temperatures are different for each compound, as listed in table 2.

3.2.1. Pattern fitting and structural models. Structure analyses were carried out by Rietveld refinements of the diffraction patterns using the Fullprof program [30]. Figure 1 shows selected examples of diffraction patterns at different temperatures and their corresponding Rietveld profiles. The whole set of diffractograms recorded and their FullProf fits are given as supplementary material (figure S1). Space groups, lattice constants, selenium atomic coordinates and Mn occupancy factors in 2c and 2d or 4d sites were determined from the Rietveld refinements for each sample at each temperature (see table 2). The parameters and space groups determined in [12] and [13] were taken as a starting point to fit the RT diffractograms. For the high temperature diffraction patterns, either below or above T_c , several space groups were considered, involving different models of cation and vacancy disorder. We tested cationic distribution involving the 2a site and also with the vacancy site participating in the exchange, but the Rietveld refinements were unsatisfactory. Thus, vacancies and Ga(2a) sites were fixed at the same positions as at RT, so that finally only $I-4$ and $I-42m$ s.g. were considered for the high temperature diffractograms. In this work the terms “disordered” and “ordered” refer to the cation distribution in either 4d or 2d and 2c sites in $I-42m$ and $I-4$ s.g., respectively.

Room temperature parameters obtained in this work are in good agreement with [12] and [13], and show a structural change at $x \approx 0.5$ as a function of composition, from ordered or partially ordered $I-4$ s.g. for $x > 0.5$ to disordered $I-42m$ s.g. for $x < 0.5$. For $x = 0.5$ good results can be obtained with either $I-4$ or $I-42m$ s.g. The same situation occurs for the diffractogram of $x = 0.24$ at $T_1 = 363$ °C. Nevertheless, in both cases, the quality refinement parameters are slightly better for $I-42m$ s.g.

According to the s.g. that gives the best fit of each diffractogram, a temperature vs. Mn concentration phase diagram can be plotted and is shown in figure 2, which includes data from all the diffraction patterns analyzed for compositions $x = 0, 0.24, 0.5, 0.77$ and 1 . Solid squares are used for the diffraction patterns fitted with $I-4$ s.g. and open squares for those fitted with $I-42m$. Intermediate situations, in which good results are obtained with either $I-4$ or $I-42m$ s.g., are denoted by crossed squares. The continuous line represents the transition temperatures found in DTA experiments in this work.

For all compositions, the high temperature (T_2) diffractograms are fitted with the $I-42m$ s.g. This implies that, at least for $x > 0.5$, the phase transition is of the order/disorder type, involving a structural change from DC to DS phases. Samples with $x = 0, 0.24$ and 0.5 present three different situations: the $x = 0.5$ sample is probably $I-42m$ at RT, unambiguously $I-4$ at T_1 and again $I-42m$ at T_2 . For $x = 0.24$ the T_1 diffractogram can be acceptably fitted with both s.g., but above T_c the structure is unambiguously disordered, with $I-42m$ s.g. The most striking case is that of $x = 0$, whose three diffractograms (RT, T_1 , T_2) are fitted within $I-42m$ s.g., which makes it difficult to elucidate the nature of the phase transition observed by DTA.

The finding of *lower* symmetry (higher order) in the T_1 diffractograms of the $x = 0.24$ and $x = 0.5$ compositions, as compared with RT ones, suggests that structural order may be *increasing* upon heating above RT, until the phase transition is approached. As we shall see

in the following discussion, this hypothesis is confirmed for all compounds of the series by the temperature evolution of lattice parameters and Mn occupation factors.

3.2.2. Lattice parameters and tetragonal distortion. Figure 3 shows the temperature evolution of the a and c lattice constants and of the tetragonal distortion parameter $\sigma = 2-c/a$ for the five samples studied. In all cases, a increases between RT and T_1 , and then contracts on crossing the phase transition, except for $x=0$, where the separation between T_1 and T_2 measurements is so large that this behaviour is probably missed. The expansion prior to T_c is more remarkable for the $I-42m$ compounds than for the $I-4$ ones. The lattice parameter c also shows a different evolution in both compositional ranges. Whereas for $x>0.5$ c increases between RT and T_1 , it decreases or remains constant for $I-42m$ compounds. At the phase transition c increases remarkably in all cases. The dependence of σ on temperature and composition is shown in figure 3(c). At RT, σ increases with increasing Mn content, from $\sigma = 0.014$, for $x=0$, to $\sigma = 0.103$, for $x=1$. As regards the temperature dependence, we see that for all compositions, except $x=1$, σ increases between RT and T_1 , and then drops significantly above T_c .

The dependence of a , c and σ with temperature and composition is attributed to the combined effect of thermal expansion and changes in the degree of structural order, both at the phase transition and before. For chalcopyrite materials it has been shown that anisotropic thermal expansion occurs, yielding in general an *increase* of the tetragonal distortion with temperature [31]. Similar effects might occur in OVC. However, the remarkably different behaviour observed for different compounds is unlikely to arise exclusively from thermal expansion and points to the additional contribution of order/disorder effects. For chalcopyrite-like materials it has been shown that a increases and c decreases with increasing order [14], which results in a close relationship between the degree of order and

the tetragonal distortion. Thus, $\sigma \approx 0$ for disordered systems and increases progressively as cations become more ordered. The same trend is followed by OVC.

Taking these considerations into account, the data of figure 3(c) can be interpreted in terms of order/disorder phenomena assuming that several stages occur sequentially upon heating above RT: i) an ordering process, enhancing the tetragonal distortion parameter σ ; ii) a decrease of this parameter due to the proximity of the phase transition; iii) the phase transition itself. The collapse of σ at T_2 for all samples indicates a transition to a disordered phase. As regards the temperature evolution of σ from RT to T_1 , the results are in close correspondence with the change in s.g. presented in figure 2. Assuming that the $x=1$ sample is completely ordered at RT, the variation of $\sigma(T)$ is considered to be the “normal” one for these compounds. The increase of σ between RT and T_1 for $x=0.77$ is attributed to the improved order within the cation distribution, still within the $I-4$ s.g. (see later discussion on occupation factors). The remarkable variation of σ for the $x=0.5$ sample can also be ascribed to ordering from RT to T_1 , now with a change of s.g. from $I-42m$ to $I-4$. As regards $x=0.24$, the increase of σ between RT and T_1 implies a tendency towards ordering that is not yet unambiguously reflected in a change of space group, but is very close to. Finally, for $x=0$ σ also increases from RT to T_1 but the increase is slight. We shall discuss these two last cases later.

For chalcopyrite materials, a critical value of $\sigma_c = 0.05$ has been established [32], so that compounds with $\sigma < \sigma_c$ at RT show a phase transition to a disordered zincblende structure at high temperature, whereas those with $\sigma > \sigma_c$ do not present such transition.

A critical σ value was also found for the compounds of our series, $\sigma_c = 0.036 \pm 0.005$, that delimits ordered from disordered structures at RT [11]. Compounds with $\sigma > \sigma_c$ present an ordered structure and $I-4$ s.g., whereas those with $\sigma < \sigma_c$ crystallize in a disordered

structure with $I-42m$ s.g. In this work we find $\sigma = 0.034$ for $x = 0.5$, which is, within error, the same as that found in [11] for that composition and confirms that $x = 0.5$ is the critical composition that separates ordered and disordered regions at RT for the as-grown materials. In order to explore the significance of this parameter further, a bibliographic revision of the lattice parameters of II-III-VI OVC has been made, and is presented in table 3. Figure 4 is a plot of c vs. a for some compounds with the DC (open symbols) or the DS structure (black dots). The solid line represents the c/a ratio corresponding to $\sigma = 0.036$. This plot suggests that $\sigma_c = 0.036$ may be a critical value for all II-III-VI OVC, not only for the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series.

We now consider the relationship between the tetragonal distortion and degree of order at high temperature. We define $\sigma_c(T)$ as the distortion corresponding to the composition that separates ordered and disordered structures at temperature T .

As seen in figure 3(c), above T_c σ falls below 0.036 for all samples analyzed, which is in good agreement with the disordered character of the high temperature phase. For the T_1 data, σ values are in correlation with the s.g. (figure 2), since for $x \geq 0.5$ the s.g. is $I-4$ and $\sigma > 0.036$, whereas for $x = 0$ the s.g. is $I-42m$ and $\sigma < 0.036$. An interesting point is that of $x=0.24$ at $T_1=363$ °C. Fitting parameters for that diffractogram give $\sigma = 0.0365$, which, within error, is coincident with the critical value at RT. On the other hand, as discussed earlier, the T_1 diffractogram of $x=0.24$ can be fitted in either $I-42m$ or $I-4$ s.g., suggesting that this composition is just at the boundary between order and disorder, i.e. $x=0.24$ is (or is very close to) the critical composition at 363 °C. This leads us to conclude that $\sigma_c(363 \text{ °C}) \simeq \sigma_c(\text{RT})$ and, by extrapolation, that σ_c may be constant with temperature. The significance of this finding is relevant, since it implies that the correlation between the tetragonal distortion and the preferred structural type holds at any temperature. Moreover, the independence of σ_c

with T implies that a single parameter governs the thermal evolution of this series: for each composition the phase transition will occur when $\sigma = \sigma_c$.

3.2.3. Mn occupation factors. A more precise insight into the physics of these processes can be derived from the Mn occupation factors. Figure 5 shows the Mn site occupation factors at RT and at T_1 obtained from Rietveld refinements in this work (for the T_2 diffractograms the s.g. has been determined to be $I-42m$ in all cases and the cations are distributed randomly in the 4d sites). In agreement with previous reports [10] at RT and for $x = 1$, Mn exclusively occupies the 2d site. As x decreases, the 2c site is increasingly populated until, for $x \sim 0.5$, x_d and x_c become equal and the structure changes to the defect stannite type with $I-42m$ s.g. A similar evolution is found for the T_1 measurements, but in this case the separation between $I-4$ and $I-42m$ regions occurs at $x \sim 0.24$. The slight decrease (increase) of x_d (x_c) observed for $x = 1$ at T_1 (536 °C) is attributed to incipient *disordering* of the Mn distribution due the proximity of the phase transition and may explain the decrease of the tetragonal distortion from RT to T_1 observed for this composition (see figure 3(c)).

For $x = 0.77$ there is no phase change between RT and T_1 , but the Mn occupation factors indicate a more ordered distribution at T_1 than at RT, as reflected by the enhancement of Mn concentration in the 2d site, at the expense of the 2c occupancy. The $x = 0.5$ composition shows the most evident example of the ordering process prior to the phase transition: x_d and x_c are equal or nearly equal at RT, whereas $x_d \gg x_c$ at T_1 . This finding is in close agreement with the change in s.g., from “ambiguous” at RT (crossed square in figure 2) to clearly $I-4$ at T_1 and also with the remarkable increase of the tetragonal distortion between RT and T_1 .

The cation distribution in the $x = 0.24$ compound apparently does not evolve from RT to T_1 , since diffractograms are fitted with $I-42m$ s.g. at both temperatures. However, we

note that neutron diffraction gives only average parameters, and is not sensitive to short-range variations in the atomic distribution. In fact, there is evidence that this compound is also undergoing an ordering process below T_c : at RT the structure is clearly the defect stannite arrangement ($I-42m$ s.g.), whereas at T_1 the Rietveld refinement results are in between $I-42m$ and $I-4$ s.g. In parallel, there is a significant σ increase between RT and T_1 . We assume that, on just a small further heating above T_1 , the sample would reach the ordered DC structure at some temperature before the phase transition to the disordered DS structure.

As regards ZnGa_2Se_4 , although the s.g. and occupation factors are the same at RT and at T_1 , a slight increase of the tetragonal distortion parameter is observed between these temperatures, which can be attributed to an ongoing ordering process, as in the rest of the compounds of the series. It is likely that T_1 (347 °C for $x=0$) is too low to allow cationic diffusion at a fast enough rate to yield long range $I-4$ s.g. in the time scale of a neutron experiment. In fact, a recent work on the thermally activated cation ordering in ZnGa_2Se_4 [33] has shown that prolonged annealing at 400°C is required to convert this compound to the DC structure. It is then reasonable to assume that in our neutron experiment ZnGa_2Se_4 has eventually become ordered at some temperature between T_1 and $T_c = 472$ °C.

In summary, the space group (figure 2), tetragonal distortion parameter (figure 3), selenium coordinates and Mn occupation factors determined from diffraction patterns collected at T_1 (table 2 and figure 4) correspond to structures more ordered than at RT, implying that an *ordering* process is activated at some temperature between RT and T_c for all members of the series, so that the phase transition reported here is of the order disorder type in all cases.

3.3. Reversibility of the phase transition.

3.3.1. Raman and optical experiments. An interesting point to discuss is to what extent the phase transition reported in this work is reversible. Pressure induced phase transitions in OVC from DC or DS to defect rock-salt structure were found to be irreversible and after releasing pressure either a defect zincblende or a quenched rock-salt structure were obtained, depending on the speed of pressure release [17-21]. However, the phase transition reported here is not of the same kind, since a fully disordered cation distribution is never reached, at least for the temperatures used in this work.

Unfortunately, we do not have neutron diffraction data of the samples after cooling down to RT, but instructive information can be obtained from other techniques. A Raman study was performed on the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ samples before and after the high temperature neutron diffraction experiments [26]. Raman spectra showed that, after cooling, long-range order had increased in all the samples, as compared with as-grown ones, so that the spectra of the after-heated samples were compatible with the ordered $I-4$ s.g. for all compositions except ZnGa_2Se_4 . (As already mentioned, later work on ZnGa_2Se_4 has shown that this compound may also be brought to DC structure through long annealing at $\sim 400^\circ\text{C}$ [33]). As an example of that behaviour, we present in the supplementary material (figure S2) the Raman spectra of the $x=0.24$ and $x=0.5$ compositions before and after the high temperature neutron diffraction experiments. In both cases the “after-heating” spectra present a better resolution and increased intensity, which is attributed to the improved structural order and to the decrease of the optical absorption at the excitation wavelength, subsequent to an ordering-induced gap shift, respectively.

In order to verify to what extent a change of the optical properties had occurred, we measured the optical absorption of selected samples, both before and after the high-temperature neutron diffraction experiment. Preliminary results for the $x=0.24$ composition

are shown in figure S3 of supplementary material. The shift of the optical absorbance of the after-heated sample toward higher energies indicates that the optical gap has increased, as expected.

3.3.2. Magnetic behaviour. The reversibility of the phase transition has been also analysed by magnetic experiments as a function of the temperature. The dc magnetic susceptibility data, collected on the series before and after the heating process, was fitted to a Curie-Weiss law $\chi = C/(T - \theta)$. The temperature range of the fit was 130 - 250 K in order to work with data at high enough temperature ($T > 5\theta$). The dependence of the Curie-Weiss temperature, θ , on the Mn content, x , is shown in figure 6 for both type of materials, that is, before and after the thermal treatment associated to the performed neutron diffraction experiments. The first set of data (before heating) agrees, within the experimental error, with a previous report [10]. A considerable reduction of the θ values is observed for the after-heating samples, except for the composition $x=1$. The Curie-Weiss temperature is a function of the x parameter through the function $\theta(x) = 2S(S+1)\sum z_i(x)J_i(x)/3k_B$ where S is the spin of the magnetic ion ($S = 5/2$ in the case of Mn^{2+}). The summation refers to the magnetic superexchange pathways, z being the number of magnetic neighbours of a given one taken as reference, and J the corresponding magnetic superexchange constant. Therefore, the negative sign of θ in the case of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series indicates predominant antiferromagnetic interactions (negative value of J).

The Curie-Weiss temperatures of diluted magnetic semiconductors usually show a decrease of θ when the concentration of magnetic atom is going down [$\theta(x) = x\theta(x=1)$].¹⁵ The increase of θ over the $x\theta(x=1)$ law along the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series (see figure 6) is then an unexpected result which indicates an increase of the global magnetic interactions.

As discussed in [10], this particular result can be explained on the basis of a creation of an additional superexchange pathway between the 2d and 2c sites as the manganese ions are promoted from 2d to 2c as x decreases from its initial value of $x=1$. The superexchange constant J associated to the magnetic pathway involving Mn atoms located in 2d and 2c sites is stronger than that exclusively relating 2d sites (the 2d-2c distance is shorter than the 2d-2d one) [10].

As a result, when comparing two samples of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series with the same manganese content x , a higher value of θ would indicate higher degree of disorder for the corresponding sample. Therefore (see figure 6) the samples after the referred thermal treatment would exhibit a higher degree of cationic order than the initial materials. A dependence of θ with the sample cooling rate used during the chemical synthesis was reported in earlier work on the subject [34].

Interestingly enough, the magnetic properties of the more disordered $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ samples, which exhibit stronger magnetic interactions, can be analyzed by obtaining these particular materials during the chemical synthesis. In fact, this is what has been done with the as-grown samples studied in this work [12,13].

4. Discussion

The preceding results show that the energy landscape of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ system, as for many ternary or multi component compounds, is complex; different states characterized by different cation distributions can exist depending on the thermal history of the samples. This variability shows up especially when there is an order/disorder phase transition at relatively low temperatures, as occurs in the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series. In such cases, the final atomic distribution is very sensitive to the experimental conditions used during the synthesis,

especially to cooling rates, so that fast cooling (as compared with cation diffusion rates at T_c) may prevent the cations from reaching their equilibrium distribution. Thus, the single crystals studied in this work, obtained from the gaseous phase by the CVT method, present a partial cation disorder that, in the case that more ordered samples were required, may be reversed upon heating the samples at moderate temperatures below T_c .

The feasibility of thermally induced cation ordering at temperatures of about 300-400 °C is corroborated by a variable-temperature Raman experiment performed on the $x=0.5$ composition [27], in which the sample was seen to transform gradually from DS to DC structure upon heating above ~ 250 °C. On further heating across T_c , a DS structure was recovered. Finally, on slowly cooling down to RT the spectrum was unambiguously characteristic of a fully ordered DC structure.

By assuming all compositions of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series reach an ordered DC structure at some temperature between RT and T_c , we conclude that the phase transition reported here is of the order-disorder type in all cases. Ordering into a DC structure is directly observed by the present high-temperature diffraction experiments (samples with $x=0.5, 0.77, 1$) or is deduced by extrapolation and comparison with other techniques ($x=0, 0.24$).

The increasing difficulty of transforming $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ compounds to the DC structure as $x \rightarrow 0$ is attributed to the similarity of the Zn^{2+} and Ga^{3+} ionic radii, Mn being the main driving force for cation ordering.

The details of the disordered cation distribution found in this series above T_c can be discussed in relation to the two-stage sequence of increasing disorder proposed by Bernard and Zunger [22] for adamantite OVC: in the first stage disorder would involve only the cation sites; in the second stage, both cations and vacancies exchange sites, leading to the defect zincblende structure. The observation of this two-stage mechanism or of a single step

of cation disorder seems to depend not only on the initial structure of the compound but also on the experimental technique used. It is outside the scope of this work to discuss the sequence of phase transitions under pressure. There is agreement, however, that a defect rock-salt structure develops at high pressure. As regards our series, Woolley et al. [25] find several consecutive phase transitions by DTA, and propose that a fully disordered zincblende-like phase occurs above $\sim 800^\circ\text{C}$, in which all cations and vacancies are randomly distributed within the cation sublattice.

In the present work we have found that only the 2c and 2d sites of *I*-4 s.g. become disordered at the phase transition, Ga ions at 2a and vacancies at 2b sites remaining fixed. This would be a previous stage occurring before the complete disorder of cation sites proposed by Bernard and Zunger.

The strong dependence of the cation distribution of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ compounds on the thermal history of each sample explains the dispersion of structural data found in the literature. Whereas our results for MnGa_2Se_4 are quite coincident with those reported previously [35], the structure of ZnGa_2Se_4 has been alternatively described as a DS or as a DC phase with low tetragonal distortion ($a = 5.50$ and $c = 11.01$ [36]; $a = 5.496$ and $c = 10.99$ [37]; $a = 5.532$ and $c = 10.914$ [38]). Woolley et al. [25] also report a fully ordered distribution for all compositions of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series at room temperature.

5. Summary and conclusions

We report several types of order/disorder phenomena in the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series of diluted magnetic semiconductors. An order/disorder phase transition is found at temperatures in the $470\text{--}610^\circ\text{C}$ range, depending on composition. According to neutron diffraction experiments, in all samples the high temperature phase corresponds to the partially disordered defect

stannite structure, with $I-42m$ space group, where the divalent cations and half of the Ga atoms are randomly distributed in the 4d crystallographic site. On the other hand, high temperature data suggest the enhancement of cation order in all samples prior to the phase transition, which is attributed to several factors: i) the partially disordered cation distribution exhibited by the single crystals grown by the CVT method, ii) the activation of cation diffusion at temperatures of the order of 300 °C, and iii) the preference of Mn atoms for the 2d crystallographic site in the $I-4$ structure.

From the thermodynamic point of view, the configuration of the as-grown samples can be described as a metastable state resulting from the existence of an order-disorder phase transition at temperatures below the synthesis temperature together with the fast cooling involved in the synthesis method itself. Depending on the transition temperature of each composition and the associated diffusion rates, the cation distribution of the disordered phase may be partially or totally quenched, leaving the system in a non-equilibrium state. Annealing at a moderate temperature below T_c provides the sample with the activation energy required to attain its minimum free energy, characterized by an ordered cation distribution. If the phase transition is crossed on cooling at slow enough rates, an ordered cation distribution may be achieved for all members of the series.

The variation in the cation distribution of the after-heated samples has a remarkable effect on the physical properties of these materials, as shown by magnetic, spectroscopic and optical techniques. This opens the way to tailoring the structural properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ materials through a carefully controlled thermal treatment as required for practical applications. For instance, the optical gap is shifted toward higher values in the more ordered samples, as observed by optical absorption measurements or deduced from the increase of Raman intensities. On the other hand, the more disordered samples of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ are interesting because they exhibit stronger magnetic interactions. Since the

electrical, optical and magnetic properties of semiconductors can be highly dependent of the degree of cation disorder, both kind of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ samples, those more disordered and those more ordered, are of interest depending on the degree of cation disorder required for a particular scientific/technological purpose.

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Table 1. The transition temperature T_c determined by DTA measurements in the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series.

x	0	0.1	0.24	0.37	0.5	0.64	0.77	0.90	1
T_c (°C)	472±2	475±2	484±2	500±2	523±2	546±2	569±2	591±2	610±2

Table 2. Results obtained from Rietveld refinements of the neutron diffraction patterns: Temperature, space group of each diffraction pattern, lattice parameters a and c , Selenium atom coordinates (x, y, z), Mn occupation factors in the 2c and 2d sites (in $I\bar{4}$ s.g.) and in the 4d site (for $I\bar{4}2m$ compounds) and quality factors R_B and χ^2 for the Rietveld refinement of each diffraction pattern.

x	T (°C)	s.g.	a (Å)	c (Å)	x _{Se}	y _{Se}	z _{Se}	OccMn(2d) OccMn(4d)	OccMn(2c)	R _B	χ^2
0	25	$I\bar{4}2m$	5.5125(1)	10.9487(1)	0.2635(1)	0.2635(1)	0.1168(1)	0		2.91	1.467
	$T_1=347$	$I\bar{4}2m$	5.5366(1)	10.9535(2)	0.2623(1)	0.2623(1)	0.1169(1)	0		4.03	2.358
	$T_2=625$	$I\bar{4}2m$	5.5407(1)	11.0251(1)	0.2624(1)	0.2624(1)	0.1174(1)	0		4.90	4.797
0.24	20	$I\bar{4}2m$	5.5367(1)	10.9533(1)	0.2630(1)	0.2630(1)	0.1165(1)	0.239(1)		4.20	1.792
	$T_1=363$	$I\bar{4}2m$	5.5701(1)	10.9372(1)	0.2614(1)	0.2614(1)	0.1166(1)	0.244(1)		4.18	3.749
	$T_2=599$	$I\bar{4}2m$	5.5627(1)	11.0398(1)	0.2618(2)	0.2618(2)	0.1172(1)	0.239(1)		5.20	4.484
0.50	35	$I\bar{4}2m$	5.5699(1)	10.9501(1)	0.2619(1)	0.2619(1)	0.1161(1)	0.484(1)		4.31	1.068
	$T_1=433$	$I\bar{4}$	5.6163(1)	10.9069(1)	0.2515(3)	0.2679(2)	0.1163(1)	0.442(1)	0.037(1)	5.42	3.690
	$T_2=620$	$I\bar{4}2m$	5.5868(1)	11.0596(1)	0.2611(1)	0.2611(1)	0.1171(1)	0.474(1)		4.78	5.537
0.77	62	$I\bar{4}$	5.6252(1)	10.8618(2)	0.2538(2)	0.2662(3)	0.1155(1)	0.660(1)	0.107(1)	8.28	1.283
	$T_1=510$	$I\bar{4}$	5.6502(1)	10.8980(1)	0.2501(2)	0.2651(3)	0.1161(1)	0.739(1)	0.032(1)	6.76	2.494
	$T_2=628$	$I\bar{4}2m$	5.6090(1)	11.0665(1)	0.2604(2)	0.2604(2)	0.1170(1)	0.739(1)		7.56	4.24
1	50	$I\bar{4}$	5.6761(1)	10.7660(1)	0.2470(1)	0.2693(2)	0.1147(1)	1	0	4.39	0.890
	$T_1=536$	$I\bar{4}$	5.6901(1)	10.8413(1)	0.2466(2)	0.2682(3)	0.1155(1)	0.935(1)	0.045(1)	4.18	2.225
	$T_2=650$	$I\bar{4}2m$	5.6272(1)	11.0706(1)	0.2588(3)	0.2588(3)	0.1172(1)	1		6.69	5.030

Table 3. Lattice parameters a and c and tetragonal distortion parameter $\sigma = 2-c/a$ of selected ternary OVC.

Compound	a (Å)	c (Å)	σ	s.g.	Ref.
CdAl₂S₄	5.5528	10.1081	0.17964	$I\bar{4}$	a
ZnGa₂S₄	5.2744	10.407	0.02689	$I\bar{4}2m$	b
CdGa₂S₄	5.5445	10.1635	0.16692	$I\bar{4}$	c
HgGa₂S₄	5.5106	10.2392	0.14191	$I\bar{4}$	c
MnGa₂S₄	5.46	10.20	0.13187	$I\bar{4}$	d
CdAl₂Se₄	5.86	10.89	0.14164	$I\bar{4}$	e
HgAl₂Se₄	5.7183	10.764	0.11757	$I\bar{4}$	c
ZnGa₂Se₄	5.5117	10.9643	0.01072	$I\bar{4}2m$	f
CdGa₂Se₄	5.743	10.756	0.127	$I\bar{4}$	g
HgGa₂Se₄	5.6930	10.8260	0.09837	$I\bar{4}$	h
MnGa₂Se₄	5.6733	10.763	0.10286	$I\bar{4}$	i
HgGa₂Te₄	6.0250	12.037	0.00217	$I\bar{4}2m$	j
MnIn₂Te₄	6.197	12.402	-0.00129	$I\bar{4}2m$	k

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Figure 1. Examples of neutron powder diffraction data collected for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ compounds at different temperatures. The dots are the experimental points, the solid line represents the calculated profile and the lower line shows the difference. The vertical marks below the diffractograms indicate the calculated positions of the Bragg reflections allowed by the corresponding space groups. For the definition of the T_1 and T_2 temperatures, see table 2.

Figure 2. Schematic phase diagram of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series. The solid line is the transition temperature T_c determined by DTA experiments (see table 1). White squares indicate $I-42m$ space group, black squares $I-4$ s.g, and crossed squares an ambiguous s.g. (i.e. a good fit is obtained with either $I-42m$ or $I-4$ s.g.).

Figure 3. (a) The lattice parameter a , (b) lattice parameter c , and (c) tetragonal distortion parameter $\sigma = 2-c/a$ obtained from neutron diffraction patterns as a function of composition and temperature. The lines are guides for the eye.

Figure 4. c vs a lattice parameter data of several OVC from the literature (see references in table 3). The solid line represents the values of c/a which correspond to $\sigma_c = 0.036$. Above and below this line the compounds have $I-42m$ and $I-4$ s.g., respectively.

Figure 5. The Mn occupation factors as a function of x determined from Rietveld refinements of the neutron diffraction patterns. Black dots represent room temperature data, and white dots represent T_1 data. For $I-4$ compounds we give occupation factors in 2c (x_c) and 2d (x_d) sites. In the case of $I-42m$ compounds we give one half of the occupation factor of Mn in 4d site. The broken lines are guides for the eye.

Figure 6. Curie-Weiss temperature, θ , of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series before (white dots) and after (black dots) the heating treatment associated to the neutron diffraction experiments. The broken lines are guides for the eye while the straight line represents $x\theta(x=1)$ (see text for details).