The influence of magnetic dilution in the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series with $0.5 < x \leq 1$

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The $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ system with $0.5 < x < 1$, which represents a magnetic dilution of the tetragonal MnGa_2Se_4 , retains the defective chalcopyrite structure of the parent compound. Neutron powder diffraction experiments and temperature dependent magnetic susceptibility measurements show that such dilution has a significant influence on the magnetic properties of the system. The distance between the closest magnetic atoms decreases from a to $a/\sqrt{2}$ Å (where a is the lattice parameter and $a \approx 5.6$ Å), making the Curie-Weiss temperature greater than the expected value. The magnetic dilution also decreases the internal distortion, so that the structure becomes closer to that of the ideal zinc-blende arrangement. Although MnGa_2Se_4 behaves as an antiferromagnet below $T_C = 6.4 \pm 0.1$ K, the magnetic properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$ suggest a glassy type behavior at low temperatures. This magnetic behavior is found to be compatible with the distribution of the Mn ions within the lattice and can be tuned by tailoring the concentration of magnetic ions. Surprisingly, the magnetically undiluted system corresponding to the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ $0.5 < x < 1$ series is not MnGa_2Se_4 , a magnetic lattice with a body centered cubic symmetry, but a structure possessing a greater number of sites available to the magnetic ions. © 2007 American Institute of Physics. [DOI: 10.1063/1.2767273]

I. INTRODUCTION

Unique results can be often obtained from the combination of two or more seemingly independent fields of research. Diluted magnetic semiconductors (DMSs), sometimes also referred to as “semimagnetic” semiconductors, constitute a beautiful example. Any known semiconductor with a fraction of its ions replaced by some magnetic cations is a potential member of this group, and these materials are of interest owing to the interplay between their semiconducting and magnetic properties. A unique and important feature of DMSs is the interaction which exists between the conduction and/or valence band electrons and the localized magnetic moments of the magnetic ions. Thus, these materials are interesting subjects for scientific research and potential device applications due to the combination of electronic, optical, and magnetic properties.¹⁻⁴

A detailed knowledge of the arrangement of the cations in the crystal lattice of DMSs is of particular significance since the physical properties (optical, electronic, magnetic, etc.) of the material are crucially influenced by the degree of atomic ordering.⁵⁻⁸ In most DMSs, the distribution of the cations is random,⁹ so that many variables follow a linear dependence with the content of the magnetic ions. This is the case with the Curie-Weiss temperature (θ).¹⁰ However, the calculation of reliable θ values is difficult in DMSs since most of them exhibit comparatively high Weiss temperatures.¹¹ As the θ values increase, the temperatures

required to perform its accurate calculation also increase and such temperatures are difficult to access experimentally.

To achieve specific requirements, various solid solutions of DMSs with different desired properties can be synthesized by varying the chemical composition.^{12,13} However, if the crystal structures of the nonmagnetic and magnetic materials are not sufficiently compatible, some problems can be encountered.¹⁴ In fact, it is found experimentally that it is generally difficult to achieve a high substitution of diamagnetic ions by magnetic ones in the host semiconductor matrix.⁹ Most of the experimental results concerning DMSs have been obtained in the range of low magnetic concentration. In this paper we analyze the magnetic and structural behaviors of a magnetic dilution of MnGa_2Se_4 in the high Mn concentration regime. Mn^{2+} is a magnetic ion with spin $S = 5/2$. The diamagnetic Zn^{2+} cation has been used for generating the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x < 1$) series. Both MnGa_2Se_4 and ZnGa_2Se_4 are semiconductors with direct gaps of around 2.5 and 2.3 eV, respectively.^{15,16}

Although the manganese ions exhibit a completely ordered distribution within MnGa_2Se_4 , the Zn cations are completely disordered in ZnGa_2Se_4 .^{17,18} This is an additional point of interest of the series under study due to the competition between the order and disorder tendencies. In addition, both crystal structures are rather compatible, with the tetragonal defective chalcopyrite structure adopted by MnGa_2Se_4 and the tetragonal defective stannite structure adopted by ZnGa_2Se_4 . The Weiss temperature for MnGa_2Se_4 is 23 K,¹⁹ a value low enough that the temperatures required to calculate accurate θ values for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x < 1$) are ac-

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cessible experimentally. Moreover, in order to increase the magnitudes of the magneto-optical effects in DMSs, it is interesting to search for materials in which the antiferromagnetic interaction between the magnetic cations is weaker, as in the case of MnGa_2Se_4 .¹⁹

We have performed neutron powder diffraction experiments to determine the degree of atomic ordering as a function of Zn/Mn dilution x in the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ system with $0.5 < x \leq 1$, complemented by dc and ac magnetic susceptibility measurements, with superconducting quantum interference device (SQUID) detection, to analyze the magnetic behavior. The magnetic properties of MnGa_2Se_4 are analyzed in this paper together with the influence of the magnetic dilution. A detailed knowledge of the structural arrangement of the atoms in the lattice is essential in order to understand the magnetic behavior of this DMS series.

II. EXPERIMENT

Orange single crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $x = 0.63(1)$, $0.77(1)$, $0.900(7)$, and 1 were obtained using the chemical vapor transport method with iodine as transport agent.^{20,21} The manganese content of each sample was determined by both magnetic and neutron powder diffraction experiments (see Sec. III below for additional information). The results obtained by these two independent methods agree within experimental error and are also in excellent agreement with the nominal value calculated from the quantity of Mn used for the chemical synthesis.

Room temperature time-of-flight neutron diffraction experiments were performed on the Polaris powder diffractometer²² at the ISIS source, UK. Thin-walled vanadium cans were used as sample containers. Diffraction data were collected in all available detector banks over a d -spacing range of $0.5 < d(\text{\AA}) < 12.0$. Neutron diffraction experiments are judged more suitable than x-ray technique to determine the distribution of magnetic ions in the series under study because the negative coherent nuclear scattering length of Mn makes it more clearly distinguishable from the other elements. The GENIE software²³ was employed for the normalization of the data and correction for sample absorption. The Rietveld analysis of the diffraction patterns was performed with the program TF14LS, based on the Cambridge Crystallographic Subroutine Library.²⁴ Refinements of the crystal structure were carried out using data in the range of $0.8 < d(\text{\AA}) < 3.2$, with an essentially constant resolution of $\Delta d/d \approx 5 \times 10^{-3}$, obtained using the highest-resolution back-scattering detectors.

ac and dc magnetic susceptibility data were collected on polycrystalline samples in the range of 1.8–300 K using a magnetometer, manufactured by Quantum Design, with SQUID detection. The ac experiments were performed under an oscillating magnetic field of 1 Oe and at frequency of 10 Hz, while the dc measurements were taken using an external magnetic field of 1 T.

FIG. 1. Distribution of cations in the unit cell of tetragonal MnGa_2Se_4 and ZnGa_2Se_4 .

III. RESULTS AND DISCUSSION

A. Structural arrangement

In order to determine the distribution of the magnetic ions within $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$, the crystal structures of the end members of the series have been taken into account. Thus, MnGa_2Se_4 crystallizes in the tetragonal space group $I\bar{4}$ with $a = 5.677(1) \text{ \AA}$ and $c = 10.761(2) \text{ \AA}$, showing a defective chalcopyrite structure.¹⁷ The structural arrangement of this material is shown in Fig. 1. The structure is defective in the sense that there are vacancies which are ordered and situated at the $2b$ ($0, 0, 1/2$) lattice site. The cations are tetrahedrally coordinated by four Se atoms located at a general position $8g$ (x, y, z). Half of the Ga cations occupy the $2a$ ($0, 0, 0$) site, while the rest are located at the $2c$ ($0, 1/2, 1/4$) crystallographic position. The Mn cations are placed at the $2d$ ($0, 1/2, 3/4$) lattice site. Thus, the crystal structure exhibits a complete ordering of the magnetic ions.

The crystal structure of the other end member of the series, ZnGa_2Se_4 , is rather similar to that reported for MnGa_2Se_4 (see Fig. 1). The structural arrangement of the atoms exhibits a tetragonal defective stannite structure, with $a = 5.5117(3) \text{ \AA}$, and $c = 10.9643(6) \text{ \AA}$ and space group $I\bar{4}2m$.¹⁸ As shown in Fig. 1, one significant difference between the crystal structure of the Zn and Mn analogs is the presence of cation disorder in ZnGa_2Se_4 . Thus, half of the Ga cations share the $4d$ ($0, 1/2, 1/4; 0, 1/2, 3/4$) position with the Zn atoms, while the remaining trivalent ions occupy the $2a$ ($0, 0, 0$) lattice site. This disorder results in the anions moving into a special position ($8i$) with $x = y$, while in the case of total order, that is MnGa_2Se_4 , the x and y coordinates of the Se atoms are different (see above). As in the case of the Mn derivative, the coordination of the cations ZnGa_2Se_4 is tetrahedral and the vacancies are located at the $2b$ ($0, 0, 1/2$) lattice site.

A major motivation of this work is to study the effects of substituting a fraction of the magnetic atoms (Mn) by diamagnetic ones (Zn). The crystal structure of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$ has been refined using the Rietveld method applied to the neutron powder diffraction data. The results of this analysis are shown in Table I (see also Figs. 2 and 3), where it is shown that all the members of

TABLE I. Mn content (x_{diff}), lattice parameters, atomic coordinates for Se [Se at general position 8g; Mn, Zn, and Ga(1) at special positions $2d$ and $2c$; Ga(2) at special position $2a$], internal distortion parameter ($\delta = [(1/4 - x_{\text{Se}})^2 + (1/4 - y_{\text{Se}})^2 + (1/8 - z_{\text{Se}})^2]^{1/2}$), occupancy factor of Mn ($2d$ and $2c$ sites), isotropic temperature factors [$\text{ITF}(2d) = \text{ITF}(2c)$], and conventional goodness-of-fit factors from Rietveld refinement of the neutron diffraction data obtained at 300 K for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x \leq 1$). Space group: tetragonal $\bar{I}4$.

x_{diff}^a	$a(\text{\AA})$	$c(\text{\AA})$	x_{Se}	y_{Se}	z_{Se}	$\delta \times 10^2$
OccMn($2d$)	OccMn($2c$)	ITF($2d, 2c$)	ITF($2a$)	ITF(Se)	R_B	R_{wp}
0.63(1)	5.593 32(1)	10.902 08(1)	0.2556(3)	0.2679(2)	0.115 44(6)	2.11 ± 0.02
0.469(6)	0.162(6)	0.365(5)	0.84(4)	0.377(9)	8.9	2.6
0.77(1)	5.620 98(1)	10.855 82(3)	0.2538(3)	0.2689(2)	0.115 02(7)	2.17 ± 0.02
0.663(5)	0.110(5)	0.25(6)	0.59(4)	0.268(9)	10.3	2.9
0.900(7)	5.648 54(1)	10.802 34(3)	0.2505(2)	0.2694(2)	0.114 76(6)	2.19 ± 0.02
0.872(4)	0.028(3)	0.40(4)	0.52(4)	0.404(8)	7.6	2.6
1.0	5.673 25(1)	10.762 94(3)	0.2476(2)	0.2703(1)	0.114 32(6)	2.31 ± 0.01
1.0	0.0	0.26(2)	0.43(4)	0.256(7)	9.4	2.4

^a x_{diff} is calculated as $\text{OccMn}(2d) + \text{OccMn}(2c)$.

the series retain the $\bar{I}4$ symmetry of the Mn end member. However, the central issue concerning the analysis of the structure in the series under study is the distribution of the magnetic cations, which could be ordered (as in the case of MnGa_2Se_4) or randomly distributed (as with the Zn cations in ZnGa_2Se_4). The distribution of the magnetic ions has been determined from the Rietveld refinement of the neutron powder patterns collected for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$, and the values are presented in Table I. As shown in this table, only the $2d$ and $2c$ lattice sites are available to the Mn ions. Therefore, the magnetic ions are partially disordered between two different lattice sites in such a way that the transference of the Mn cations from the $2d$ to the $2c$ lattice site increases as the magnetic dilution progresses. As discussed in the next section, this lack of complete order significantly influences the magnetic properties of the system. Moreover, the values of the tetragonal parameters a and c are depicted in Table I as a function of x . While a increases with the Mn content, c decreases. This is in contrast with the nearly constant value of c detected in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 \leq x < 0.5$, which exhibit a completely random distribution of the Zn cations.²⁵ The increase of c/a with decreasing x suggests a tendency to an increase in cation ordering as the

concentration of Mn progresses.²⁶ This conclusion also agrees with the distribution of the magnetic ions determined for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$ (see Table I).

The partial substitution of Zn by Mn does not change the population of the $2a$ lattice site and, as expected, the bond distance $\text{Ga}(2a)\text{--Se}$ in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$ is not significantly affected by the substitution process (see Table II). Its value is in agreement with that reported for ZnGa_2Se_4 [$2.4204(10)$ Å] (Ref. 18) and MnGa_2Se_4 [$2.42(2)$ Å].¹⁷ By contrast, the distance $\text{Mn, Zn, Ga}(2d)\text{--Se}$ increases with x . This is to be expected, since the Mn–Se bond distance in this type of materials is larger than the Ga–Se and (Zn, Ga)–Se distances. The bond distances Mn–Se and (Zn, Ga)–Se have been reported to be 2.55(2) and 2.4365(5) Å, respectively, in MnGa_2Se_4 (Ref. 17) and ZnGa_2Se_4 .¹⁸ More interestingly, the $\text{Mn, Zn, Ga}(2c)\text{--Se}$ distance increases smoothly when x is decreased, in good agreement with an increase of the Mn content in the $2c$ crystallographic site as x decreases.

A detailed knowledge of the atomic structure of such defective compounds is of interest due to the sensitivity of the electronic properties to the internal distortion,²⁷ represented by the displacement of the anion from its position

FIG. 2. Least-squares fit to the powder neutron diffraction data collected at ambient temperature from $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $x=0.63$. The solid line denotes the calculated profile and the dots represent the experimental data points. The lower trace shows the difference (measured minus calculated) divided by the estimated standard deviation on the experimental data points. The thick marks along the top of the figure illustrate the calculated positions of all the Bragg reflections allowed by $\bar{I}4$ symmetry.

FIG. 3. Least-squares fit to the powder neutron diffraction data collected at ambient temperature from MnGa_2Se_4 . The solid line denotes the calculated profile and the dots represent the experimental data points. The lower trace shows the difference (measured minus calculated) divided by the estimated standard deviation on the experimental data points. The thick marks along the top of the figure illustrate the calculated positions of all the Bragg reflections allowed by $\bar{I}4$ symmetry.

TABLE II. Main bond distances obtained from Rietveld refinement of the neutron diffraction data taken at 300 K for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x \leq 1$). Space group: tetragonal $I\bar{4}$. The experimental Curie-Weiss constant θ_{exp} and the manganese content x_{mag} have been calculated from magnetic susceptibility data (see text). $\theta_{\text{excess}} = \theta_{\text{exp}} - x\theta_{x=1}$, while T_f is the temperature associated with the low temperature magnetic anomaly (Neel temperature for MnGa_2Se_4).

x_{diff}^a x_{mag}	$d[2d\text{-Se}](\text{\AA})^b$ $T_f(\text{K})$	$d[2c\text{-Se}](\text{\AA})^b$ $\theta_{\text{exp}}(\text{K})$	$d[2a\text{-Se}](\text{\AA})^b$ $\theta_{\text{excess}}(\text{K})$
0.63(1)	2.503(1)	2.425(1)	2.424(1)
0.63 ± 0.02	2.45 ± 0.05	-39 ± 2	-26 ± 3
0.77(1)	2.519(1)	2.423(1)	2.425(1)
0.75 ± 0.02	3.40 ± 0.05	-27 ± 2	-11 ± 3
0.90(1)	2.537(1)	2.415(1)	2.420(1)
0.88 ± 0.02	4.75 ± 0.05	-22 ± 2	-3 ± 3
1.0	2.556(1)	2.409(1)	2.416(1)
1.0	6.4 ± 0.1	-21 ± 2	0

^aMn content determined from diffraction data.

^bSe at general position 8g; Mn, Zn, and Ga(1) at special positions 2d and 2c; Ga(2) at special position 2a; vacancy at special position 2b.

within an ideal zinc-blende structure. The tetragonal defective stannite and chalcopyrite structural arrangements can both be derived from the cubic zinc-blende structure by doubling the unit cell parameter c , considering two different cations rather than one and introducing vacancies into the lattice. As a consequence of the lowering of symmetry, the anions are forced to relax with respect to $(1/4, 1/4, 1/8)$, the ideal position of the anion in the zinc-blende structure. The coordinates of the Se atoms ($x_{\text{Se}}, y_{\text{Se}}, z_{\text{Se}}$) are shown in Table I for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$. The dependence of the internal distortion parameter, defined as $\delta = [(1/4 - x_{\text{Se}})^2 + (1/4 - y_{\text{Se}})^2 + (1/8 - z_{\text{Se}})^2]^{1/2}$, has been calculated for this series as a function of the manganese content and is shown in Table I. The decrease of δ with x indicates that the displacement of the anion from its position in the ideal zinc-blende structure decreases as the proportion of magnetic ions diminishes. The same tendency occurs for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 \leq x < 0.5$ when the Zn cations are progressively substituted by Mn ions.²⁵ These results indicate that when starting the dilution from either ZnGa_2Se_4 or MnGa_2Se_4 , the crystal structure of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 < x < 1$ series tends to minimize the internal distortion, becoming closer to that of the ideal zinc-blende arrangement (see Fig. 4). Such a mini-

FIG. 4. Internal distortion δ for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0 \leq x \leq 1$. The parameter δ represents the displacement of the anion from its position within an ideal zinc-blende structure, while ($x_{\text{Se}}, y_{\text{Se}}, z_{\text{Se}}$) are the atomic coordinates of selenium in the series under study.

FIG. 5. Evolution of the inverse of the dc magnetic susceptibility with temperature for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$, under an external magnetic field of 1 T.

mum is reached for intermediate values of the dilution ($x \approx 0.5$).

B. Magnetic behavior

The magnetic properties of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series are determined by the presence of the magnetic manganese ion. MnGa_2Se_4 has been reported to order as an antiferromagnet below $T_c = 6.4 \pm 0.1$ K, with $\theta = -23 \pm 2$ K.¹⁹ Superexchange has been proposed as the main mechanism to explain the magnetic interaction between Mn cations in Mn-based DMSs.^{28,29} The members of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series with $0.5 < x \leq 1$ behave as paramagnets in the high temperature region, as shown by the dc magnetic susceptibility data depicted as a function of temperature in Fig. 5. In order to calculate the Curie constant C and the temperature correction θ , the magnetic data have been fitted to a Curie-Weiss law $\chi = C/(T - \theta)$ over the temperature range of 130–250 K. A nonzero value of θ indicates the presence of magnetic interactions within the paramagnetic phase. The mathematical expression for the Curie constant is $C = xNg^2\mu_B^2S(S+1)/3k_B$, where x represents the fraction of magnetic ions, N is Avogadro's constant, g is the Landé factor, μ_B the Bohr magneton, S the spin of the magnetic ion ($5/2$ for Mn^{2+}), and k_B is Boltzmann's constant.³⁰ The g factor can be calculated from the experimental Curie constant $C_{x=1}$ of MnGa_2Se_4 , since this compound has $x=1$ and the only unknown in the above expression for the Curie constant is the Landé factor g . The content of Mn in each sample can be obtained from this magnetic data since C is a function of x [the estimated accuracy of the method is $\sim \pm 5\%$ (Ref. 31)]. The Mn content of the members of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$ series calculated from the magnetic data, x_{mag} , are in good agreement with those obtained from analysis of the neutron powder diffraction, x_{diff} . Both values are shown in Table II for comparison.

Depending on the temperature range used for fitting the experimental susceptibility data to the inverse of a Curie-Weiss law, the θ values can be very different for a given

FIG. 6. Thermal dependence of the in-phase χ' (circles) and out-of-phase χ'' (triangles) components of the ac magnetic susceptibility for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$.

series of DMSs. Following that law, $1/\chi = -\theta/C + T/C$, the agreement between the slope $1/C$ calculated from both diffraction and magnetic data has been used as a criterion to support the choice of temperature range used for the fitting of the magnetic data and, as a consequence, the reliability of the resultant θ values.²⁵ The Curie constant C can be calculated from the diffraction data using the Mn content obtained from such data, x_{diff} , and the mathematical expression of C , which is a function of x (see above). The results for θ are shown in Table II. The negative values are indicative of predominant antiferromagnetic interactions in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$.

In the bibliography related to DMSs, Curie-Weiss temperatures are typically reported over a limited range of composition, frequently in the low concentration regime of magnetic ions. These θ temperatures show a (usually linear) reduction with the concentration of magnetic ions, that is $\theta(x) = x\theta_{x=1}$ where $\theta_{x=1}$ represents the Curie-Weiss temperature for the undiluted compound.¹⁰ This decrease does not occur in the case of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$ (see Table II). An excess over the value expected for θ can be calculated following the expression $\theta_{\text{excess}}(x) = \theta_{\text{experimental}}(x) - x\theta_{x=1}$. The results of these calculations are shown in Table II for the series under study. It is clear that θ_{excess} increases as x decreases, in accord with the increase in the number of magnetic ions promoted from the $2d$ to the $2c$ crystallographic sites as x is decreased (see Table I). The presence of magnetic ions in both the $2d$ and $2c$ lattice sites gives rise to $\text{Mn}^{(2d)}\text{-Se-Mn}^{(2c)}$ superexchange pathways, which are shorter than those $\text{Mn}^{(2d)}\text{-Se}\cdots\text{Se-Mn}^{(2d)}$ ones present in MnGa_2Se_4 . In fact, the magnetic constant corresponding to $\text{Mn}^{(2d)}\text{-Mn}^{(2d)}$ contacts has been estimated as 0.1–0.5 K for MnGa_2Se_4 ,¹⁹ while that associated with the $\text{Mn}^{(2d)}\text{-Mn}^{(2c)}$ contacts has been calculated as 12.2 K for the magnetic system $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$.³²

The low temperature magnetic behavior of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x \leq 1$) is illustrated in Fig. 6. MnGa_2Se_4 exhibits a broad peak centered at 7.9 ± 0.5 K. The out-of-phase component of the ac magnetic susceptibility χ'' is three orders of magnitude smaller than χ' and shows no anomaly for this compound. The temperature dependence of both χ' and χ'' indicates that antiferromagnetic ordering occurs in MnGa_2Se_4 below $T_C = (d\chi/dT)_{\text{max}} = 6.4 \pm 0.1$ K, in ex-

FIG. 7. Distances between the manganese ions as a function of the degree of atomic dilution in $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x \leq 1$. On the right-hand side of the figure, the equations used to calculate those Mn–Mn distance are shown (a and c are the unit cell parameters). On the left-hand side the J_i superexchange magnetic constants corresponding to those distances are presented.

cellent agreement with a transition temperature of 6.4 ± 0.1 K calculated from specific heat measurements.¹⁹ Interestingly, the specific heat data collected on MnGa_2Se_4 show that approximately 30% of the magnetic entropy is gained above the Neel temperature, indicating that short-range order persists at temperatures much higher than the ordering temperature.

In order to understand this experimental result, it is necessary to analyze the main magnetic superexchange pathways acting in MnGa_2Se_4 . The associated magnetic constants are J_2 , along $[100]$ and $[010]$, J_3 , along $[1/2, 1/2, 1/2]$, and J_4 , along $[110]$. For simplicity we have used the convention of placing the reference magnetic atom at the $(0,0,0)$ crystallographic position. The exchange constants J_2 and J_4 involve magnetic interactions within the xy plane. Thus, the magnetic constant J_2 relates Mn atoms located at the corners of the unit cell along the x or y axis, while J_4 links Mn atoms situated along the diagonal of the xy plane. Therefore, the only way of propagating the magnetic interaction in the third dimension, the z axis, is the magnetic pathway associated with J_3 . This relates the reference Mn atom situated in one corner of the unit cell to another Mn located at the body center position. The distance between Mn atoms linked by J_2 is shorter than those linked by J_3 (see Fig. 7). Only the order of magnitude of the superexchange constants is known for MnGa_2Se_4 (0.1–0.5 K).¹⁹ The exchange constants for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$, with a similar crystal structure, have been reported as $J_2/k_B = -0.2$ K, $J_4/k_B = -0.4$ K, and $J_3/k_B = -0.1$ K.³² Therefore, the magnitude of the exchange interactions is expected to be higher within the xy plane than along the z axis. This spatial anisotropy is consistent with the presence of short-range order, as detected by the heat capacity measurements at temperatures much higher than the ordering temperature (see above). Moreover, some degree of magnetic frustration is present in MnGa_2Se_4 . An antiferromagnetic ordering between nearest neighbors without frus-

tration is possible within the xy plane. The difficulty arises when attempting to propagate the antiferromagnetic ordering along the third dimension, the z axis, through the magnetic ion situated at the body center position. A collinear antiferromagnetic three dimensional ordering without frustration is not possible due to the spatial arrangement of the Mn atoms.

We now consider how the partial substitution of the Mn atoms by diamagnetic ones affects the magnetic configuration of the parent compound. To address this issue we have performed ac magnetic susceptibility experiments on the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series with $0.5 < x < 1$. The evolution of the in-phase component of the ac magnetic susceptibility data, χ' , also shows a maximum as a function of the temperature in all the members of the series (see Fig. 6). The magnetic dilution creates additional superexchange pathways due to the migration of magnetic ions from the $2d$ to the $2c$ lattice positions (see Table I). The additional exchange constants are J_1 along $[1/2, 1/2, 0]$ associated with Mn–Se–Mn interactions; $J_{2'}$, along $[0, 0, 1/2]$ and $J_{4'}$, along $[1, 0, 1/2]$ and $[0, 1, 1/2]$. Again, for simplicity, we place the reference magnetic atom at the $(0, 0, 0)$ crystallographic position. The distances between Mn atoms along the main magnetic superexchange pathways have been calculated as a function of the Mn content for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ (see Fig. 7). The Mn–Mn distances associated with J_1 , J_2 , J_4 , and $J_{4'}$ decrease with x , predicting an increase in these magnetic constants as the concentration of the magnetic atoms decreases. By contrast, as the Mn–Mn distance corresponding to $J_{2'}$ and J_3 increases when the internal variable x is reduced, a decrease of these superexchange constants with the Mn content would be expected. Both $J_{2'}$ and J_3 are associated with the propagation of the magnetic interaction along the z axis. The evolution of $\chi'(T)$ for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x < 1$) shows a decrease of T_f (the temperature associated with the magnetic anomaly) with x and a loss of the broad nature of the maximum shown in MnGa_2Se_4 (see Fig. 6). On the other hand, it is interesting to note that, due to the promotion of Mn ions from $2d$ to $2c$ lattice sites, the magnetic archetype of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x < 1$) is not that corresponding to MnGa_2Se_4 , a magnetic lattice with a body centered cubic symmetry, but rather a structure with more lattice sites available to the manganese cations (see dark circles in ZnGa_2Se_4 , Fig. 1).

At this point, it is significant to remark the existence, in all the members of the series except MnGa_2Se_4 , of a non-negligible out-of-phase component of the ac magnetic susceptibility χ'' (see Fig. 6). This magnitude exhibits a sharp increase with decreasing temperature near T_f . Although MnGa_2Se_4 behaves as an antiferromagnet, the thermal dependence of both χ' and χ'' for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x < 1$) is consistent with the presence of a spin-glass-like magnetic state at low temperatures.^{9,33} The interactions between magnetic moments in spin glasses are frequently in conflict with each other due to some form of frozen-in disorder, so that they exhibit a “freezing transition” to a state in which the spins are aligned in random directions. In order to determine the spin-freezing temperature T_f in a consistent manner, straight lines were fitted on either side of the transition through the data points. The transition temperature was taken to be the point of intersection of these two lines.³⁴ The values

of T_f determined in this way are shown in Table II and demonstrate a decrease of T_f as x is decreased. For a large number of II–VI compounds, the spin-freezing temperature T_f can be fitted to a power law of the type $T_f \sim x^{n/3}$, which is a function of the concentration of magnetic ions.³⁵ In this expression the exponent n relates the dependence of the superexchange interaction J with the distance between magnetic atoms.³⁵ In the case of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$, the exponent is determined to be $n \sim 5.6$. The value of n is found to lie in the range from 5 to 6.8 for $\text{II}_{1-x}\text{Mn}_x\text{VI}$ compounds.³⁵ Therefore, the result obtained for $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$ illustrates the applicability of this approach for a nonrandom distribution of magnetic ions and validates its use outside the limit of the dilute regime to which it is usually restricted.³⁵

Further studies are in progress to obtain a deeper understanding of the magnetic behavior exhibited by $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ with $0.5 < x < 1$ at low temperatures, including the variation of the magnetic susceptibility with the frequency of the ac field, the thermal evolution of the magnetization in the presence or absence of a magnetic field, and the variation of the heat capacity with the temperature.

IV. CONCLUSIONS

The end member of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x \leq 1$) series, MnGa_2Se_4 , exhibits a completely ordered distribution of the magnetic ions on the $2d$ lattice site of the tetragonal space group $I\bar{4}$. However, the partial substitution of Mn by Zn produces a partially, rather than totally, disordered distribution of the magnetic ions on the $2d$ and $2c$ lattice sites of the defective chalcopyrite structure. The increase of the unit cell parameter c/a as the Mn content decreases is consistent with the increased degree of cation disorder as the magnetic dilution progresses. The magnetic dilution also decreases the internal distortion, the structure becoming closer to that of the ideal zinc-blende structure. Another consequence of the partial substitution of Mn by Zn is that the minimum distance between magnetic atoms decreases from a to $a/\sqrt{2}$ Å, increasing the strength of the magnetic constant between nearest neighbors. This fact, together with the increase in the population of magnetic ions at the $2c$ lattice site, causes θ_{excess} , the excess over the value expected for the Curie–Weiss temperature, to increase with the magnetic dilution.

The low dimensional magnetic behavior of MnGa_2Se_4 detected at temperatures higher than that of the antiferromagnetic ordering has been explained in terms of the spatial anisotropy of the magnetic interactions within and perpendicular to the xy plane. Although MnGa_2Se_4 orders as an antiferromagnet below $T_C = 6.4 \pm 0.1$ K, the presence of a cusplike anomaly in the evolution of both the in-phase, χ' , and the out-of-phase, χ'' , components of the magnetic susceptibility suggests a glassy type magnetic behavior of $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0.5 < x < 1$) at low temperatures. This magnetic behavior is consistent with the distribution of the Mn ions in the lattice. Interestingly, although the Curie–Weiss temperature increases as x decreases, the spin-freezing temperature T_f decreases as x decreases. The magnetic archetype of the series under study is not MnGa_2Se_4 , where the

manganese cations are distributed on a body centered cubic lattice, but a system possessing a greater number of sites available for the magnetic ions.

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