

Disorder in $(\text{Zn}_{1-x}\text{Mn}_x)_3\text{As}_2$ and its consequences on impurity conduction and magnetic properties

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Abstract. Disorder of stacking of vacant sites in the crystal structure of II_3V_2 compounds, including the diluted magnetic semiconductor $(\text{Zn}_{1-x}\text{Mn}_x)_3\text{As}_2$, is investigated. Special attention is paid to the remanent disorder at temperatures much below the order–disorder phase transition temperature T_{ph} . Dependences of T_{ph} and the activation energy of hopping conductivity on composition are analysed. Good agreement is obtained between theory and experimental results for the phase transition and the hopping conductivity, occurring in two quite different temperature regions. It is suggested that the remanent structural disorder leads to generation of complex centres with a large magnetic moment and a large amount of internal spin degrees of freedom. We call these centres clusters of polarization. Conditions of freezing-in of a system of interacting clusters of polarization is analysed. A way to obtain the parameters describing these centres and their interaction is discussed.

1. Introduction

Solid solutions of zinc arsenide and manganese arsenide, $(\text{Zn}_{1-x}\text{Mn}_x)_3\text{As}_2$ (ZMA), represent a new class of semimagnetic semiconductors based on II_3V_2 compounds. These alloys have interesting magnetic properties, including freezing of the moments above 200 K [1] and the appearance of a low-temperature spin-glass (SG) phase below 4 K [2].

A specific feature of II_3V_2 compounds is that a quarter of the sites in the metallic sublattice are vacant. In their low-temperature α modifications the stacking of the vacant sites (VSs) has long-range ordering while in the high-temperature β -phases the VS stacking is disordered. The order–disorder phase transition has been found in three of the four known II_3V_2 semiconductors, i.e. in Zn_3As_2 , Cd_3As_2 and Zn_3P_2 [3–5]. The α -phases of all these materials are very similar. Atoms from the second group ('metals' or M atoms) are tetrahedrally coordinated by the atoms of the V group ('non-metals' or Y atoms), whereas the Y atoms are sixfold coordinated by the M atoms occupying six out of the eight sites ('b sites') localized at corners of a slightly distorted cube. Two sites remain vacant ('a sites') [5].

The chemical bond of II_3V_2 compounds is the multicentre bond. It has been studied in Zn_3P_2 [6], treating the Y atom with its nearest M and VS neighbours as the smallest structural unit (figure 1(a)). It was shown that each Y atom contributes five electrons and each M atom half an electron to the multicentre bond. The cohesive energy W_c of this unit was calculated and found to be in good agreement with experimental data.

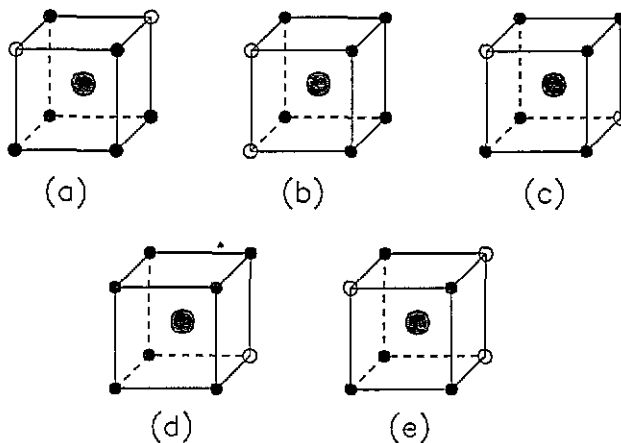


Figure 1. Different configurations of M atoms (full circles) and VSs (open circles) from the first coordination of a Y atom (large shaded circles) connected with the disorder of VSs.

In the present paper we study the order–disorder phase transition temperature T_{ph} and the remanent disordering of VSs in II_3V_2 materials, including ZMA, using the Bragg–Williams approximation. A unified approach to these compounds and alloys is possible because the crystal structure of ZMA is isomorphic to that of Zn_3As_2 with x at least up to 0.135 [7]. Special attention is paid to the remanent disorder, i.e. the deviation from the long-range ordering in the stacking of VSs at temperatures $T \ll T_{ph}$. The remanent disorder of VSs strongly influences the low-temperature conductivity of ZMA, because it leads to effective generation of impurity centres. A detailed comparison between the theoretical and experimental dependences of T_{ph} and the activation energy E_a of the hopping conductivity on x is made. The remanent disorder is interesting also for a better understanding of the unusual magnetic properties of ZMA. The disorder of VSs results in two different systems of paramagnetic atoms, formed by Mn atoms at the a and b sites. The consequences of this situation on the low-field magnetic susceptibility of ZMA are analysed.

2. Order–disorder transition in the II_3V_2 compounds

2.1. Definition of the model

In figure 1(a) is shown the metallic coordination of a Y atom in the case of ideal ordering of VSs. Disorder of VSs may lead to the situation when the number j of the M atoms, nearest to the Y atom is not changed (figures 1(b) and 1(c)) or it is changed (see, e.g., figures 1(d) and 1(e)). The Y atoms with coordination j are denoted as $j\text{Y}$ atoms.

Below we use the pair approximation of the multicentre bond. On the one hand, we must take into account the saturation property of the covalent bond. If interactions are exactly two centred, then this property would mean that a Y atom interacts with only six neighbouring M atoms. On the other hand, for $j > 6$ the multicentre character of the chemical bond leads to a situation when each of seven or eight M atoms (the case of $j = 8$ is not shown in figure 1 but it is possible with a small probability; see the end of this section) from the first coordination of a Y atom can be regarded as superfluous with equal probability, 6/7 or 6/8, respectively. This ambiguity can be removed if we assume firstly that a Y atom interacts with all neighbouring M atoms but the interaction energy E_j of a pair M– $j\text{Y}$ depends on coordination j and secondly that the saturation property of the

multicentre bond in the pair approximation can be treated as conservation of the cohesive energy defined now as $W_c = jE_j$ when j is increased above the value 6. Consequently, using these assumptions we obtain $E_7 = 6E_6/7$ and $E_8 = 6E_6/8$. Opposite to this case, when $j < 6$, simple relations between E_j and E_6 cannot be found from the assumptions made above. Instead, we use another simplification, namely that $E_j = E_L$ for all $j < 6$. The validity of this approximation will be verified below.

As evident from figure 1, disorder of VSs should lead also to some additional distortions of metallic coordination of a Y atom (not shown in figure 1) which may exert some influence on the M-Y interaction energy. Below we demonstrate that such an influence is small. For instance the mean variation $\langle \Delta E_6/E_6 \rangle$ in the M-6Y interaction energy associated with such distortions can be estimated as $\langle \Delta E_6/E_6 \rangle \sim p_b \Delta d/d$ where $p_b \approx 0.03$ is the probability of finding the configuration shown in figure 1(b) in conditions of complete disorder and $\Delta d/d \approx 0.13$ is the relative variation in the M-6Y distance (when the Y atom is shifted from the centre of the cube) which is maximal for this configuration in comparison with those shown in figures 1(a) and 1(c). We obtain that the value of $\langle \Delta E_6/E_6 \rangle \approx 0.4\%$ is negligible compared with for example that of $(E_6 - E_7)/E_6 \approx 14\%$.

We define the long-range order parameter as usual [8, 10]:

$$s = (p - p_{min}) / (p_{max} - p_{min}) \quad (1)$$

where p is the probability of finding the a site empty ($p_{max} = 1$, $p_{min} = 1/4$).

In the pair approximation the energy of the crystal is

$$U = m_L E_L + m_6 E_6 + m_7 E_7 + m_8 E_8. \quad (2)$$

Here $m_j = 4N_b P_j$ is the number of the M- j Y pairs (if $j = L$, m_L is the number of the pairs with $j < 6$), N_b is the number of the b sites (for Zn_3As_2 equal to $2.9 \times 10^{22} \text{ cm}^{-3}$), and $P_j = 6^{-1} \sum_{k+l=j} (k+l) P_{kl}$ is the probability of finding an M- j Y pair. $P_{kl} = P_k(b)P_l(a)$ is a product of the probabilities

$$P_k(b) = 4^{-6} C_k^6 (3+s)^k (1-s)^{6-k} \quad (3)$$

and

$$P_l(a) = 4^{-2} C_l^2 (1-s)^k (1+3s)^{2-l} \quad (4)$$

for a situation that k sites from the six b sites and l from the two a sites of the first coordination sphere of the Y atom are occupied by M atoms, respectively. In equations (3) and (4), C_i^j are the binomial coefficients.

The entropy S of the crystal is determined by the number of different rearrangements of M atoms over a and b sites, as usual [8]. Then the equation for the order parameter may be obtained by minimizing the free energy $F = U - TS$:

$$\tau \log\{(3+s)(1+3s)/[3(1-s)^2]\} = w(s). \quad (5)$$

Here $\tau = kT/|E_6|$ is a dimensionless temperature and $w(s)$ or the energy of disordering is

$$w(s) = 16[(1-\beta)(P'_{60} + P'_{51} + P'_{42}) + (1-7\beta/6)(P'_{52} + P'_{61}) + (1-8\beta/6)P'_{62}] \quad (6)$$

where $\beta = E_L/E_6$ and $P'_{kl} = dP_{kl}/ds$. The value of β is determined mostly by the crystal structure and can be taken as a constant within the compounds and alloys considered.

The interpretation of solutions of equation (5) can be made by analogy with binary metallic alloys [8]. This equation has a trivial solution, $s = 0$, which in the region of $T > T_{ph}$ is the only solution. In the temperature range $T < T_{ph}$, two non-trivial solutions also exist, a stable branch, $s'(T) < 0$, and an unstable branch, $s'(T) > 0$, where $s'(T) = ds/dT$. Hence, at $T = T_{ph}$ there is a first-order phase transition, with the leap

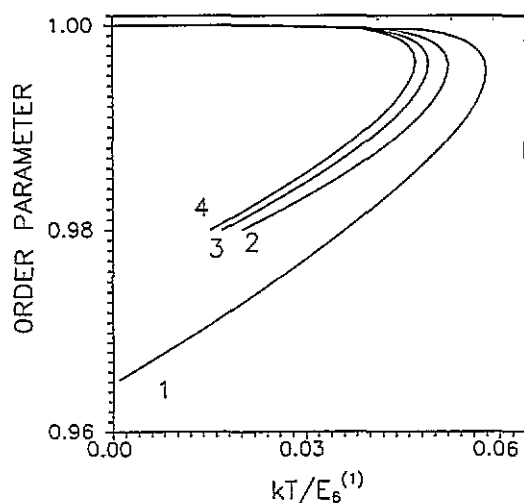


Figure 2. Temperature dependence of the order parameter s for ZMA with $x = 0$ (curve 1), 0.05 (curve 2), 0.10 (curve 3) and 0.15 (curve 4).

of the order parameter from an almost ordered state ($1 - s \approx 4 \times 10^{-3}$) to a completely disordered phase ($s = 0$). The function $s(T)$, excluding the trivial solution, is presented in figure 2 (see the case when $x = 0$). Because β is constant, the dimensionless temperature τ_{ph} at the transition point is also constant. Using the values of $T_{ph}^* = 1153$ K [5] and $|E_6^*| \approx W_c/6 = 1.72$ eV [6] for Zn_3P_2 , we get $\tau_{ph} = 0.058$. The value of $\beta \approx 1.16$ is selected in equation (6) so that the value of τ_{ph} is equal to that determined above. The values of E_6 for other II_3V_2 compounds can be obtained with the formula

$$E_6 = (T_{ph}/T_{ph}^*)E_6^*. \quad (7)$$

Using $T_{ph} = 945$ K and 868 K for Zn_3As_2 and Cd_3As_2 [5] we obtain $|E_6| = 1.41$ eV and 1.29 eV, respectively, for these compounds. For Cd_3P_2 , $|E_6| > 1.51$ eV because in this compound no phase transition has been observed up to the melting temperature $T_m = 1012$ K [3–5].

The smallness of $1 - s$ at $T \leq T_{ph}$ means that in this temperature interval the interactions in the M–5Y, M–6Y and M–7Y pairs play the main role. This justifies the simplification $E_j = E_L$ made above (practically $E_L = E_5$).

2.2. Order–disorder transition in ZMA

Since ZMA is isomorphic to Zn_3As_2 , disordering of VSs may be described similarly to all compounds mentioned above, except that the binomial distribution of the probabilities (3) and (4) should be changed to a polynomial distribution [9]. As independent variables we use the relative concentrations of Zn and Mn atoms at the a sites: $n_1 = N_1/N_b$ and $n_2 = N_2/N_b$, respectively. Here and thereafter all values with the index 1 are attributed to the Zn atoms, and all values with the index 2 to the Mn atoms. The minimization of the free energy must be done over the parameters n_1 and n_2 . This leads to a pair of equations

$$\tau \log\{3n_i(n_i + n_k)/[(\xi_i - n_i)(1 - 3n_i - 3n_k)]\} = -w_i \quad i \neq k = 1, 2 \quad (8)$$

where $\xi_1 = 1 - x$, $\xi_2 = x$ and $w_i = w(s) + \psi_i(n_1, n_2)$ is the energy of disordering of VSs by the i th type of atom. The function $\psi_i(n_1, n_2)$ can be expressed as

$$\psi_i(n_1, n_2) = -4(g - 1)[(1 - \beta)\partial P_6^{(2)}/\partial n_i + (6/7 - \beta)\partial P_7^{(2)}/\partial n_i + (6/8 - \beta)\partial P_8^{(2)}/\partial n_i] \quad (9)$$

$$i = 1, 2$$

with $g = E_6^{(2)}/E_6^{(1)}$ and $\tau = kT/|E_6^{(1)}|$. The probability of finding a pair of Mn- j A is

$$P_j^{(2)} = 6^{-1} \sum_f \sum_s (k_2 + l_2) P(k_1 k_2 l_1 l_2). \quad (10)$$

The summation \sum_f is over the values of $k_2 + l_2 = 1 \dots j$, and \sum_s is over all values of $k_1 + l_1 = j - k_2 - l_2$, so that $0 \leq k_1 + k_2 \leq 6$ and $0 \leq l_1 + l_2 \leq 2$. In $P(k_1 k_2 l_1 l_2) = P(k_1 k_2)P(l_1 l_2)$,

$$P(k_1 k_2) = 6!/[k_1!k_2!(6 - k_1 - k_2)!](1 - x - n_1)^{k_1}(x - n_2)^{k_2}(n_1 + n_2)^{6 - k_1 - k_2} \quad (11)$$

$$P(l_1 l_2) = 2!/[l_1!l_2!(2 - l_1 - l_2)!](3n_1)^{l_1}(3n_2)^{l_2}(1 - 3n_1 - 3n_2)^{2 - l_1 - l_2} \quad (12)$$

are the probabilities that k_1 and k_2 from six b sites and l_1 and l_2 from two a sites of the first coordination sphere of the As atom are occupied by Zn (index 1) and Mn (index 2) atoms, respectively. The order parameter is related with n_1 and n_2 as

$$s = 1 - 4(n_1 + n_2). \quad (13)$$

For $g < 1$ and $x > 0$ the non-trivial solutions of equations (8) have two branches of $n_i(T)$ (figure 3). They are also presented in figure 4 as functions of s . The temperature of the order-disorder transition is shifted to lower values (see figure 2) corresponding to T_{ph} determined by thermographic measurements (see figure 5). The function $T_{ph}(x)$ calculated with equations (8) agrees completely with the experimental data if the value of g is 0.64.

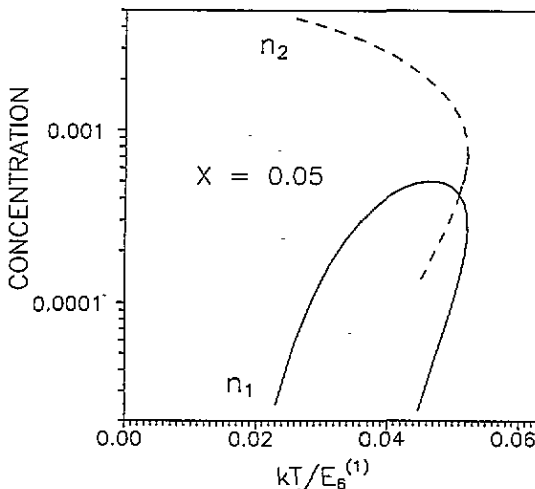


Figure 3. Temperature dependences of n_1 and n_2 for ZMA with $x = 0.05$.

3. Generation of impurity centres and application to impurity conduction of ZMA

Below the order-disorder transition temperature, $1 - s$ has a very small but finite value and the ordering of VSs is not complete. The overwhelming majority of M atoms at the a

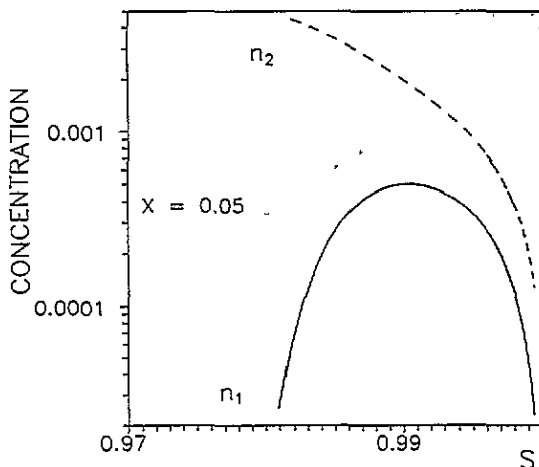


Figure 4. Concentrations n_1 and n_2 versus the order parameter s .

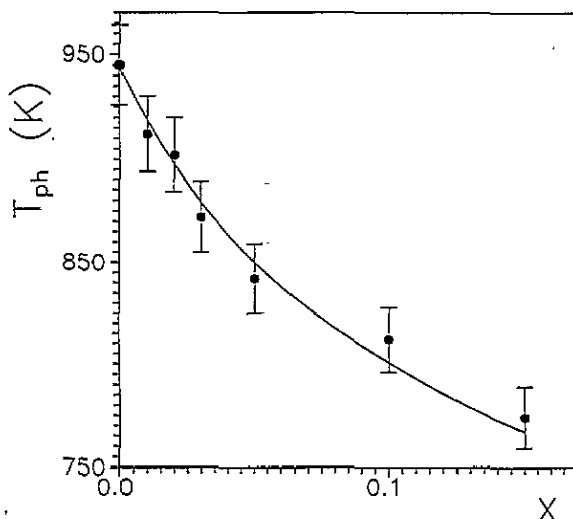


Figure 5. Transition temperature T_{ph} versus x for ZMA; ●, experimental values; —, calculated results.

sites in this temperature region are far from the nearest empty b site. Therefore, relaxation of the order parameter to the equilibrium value when the temperature is lowered must be realized by diffusion of M atoms towards the empty b sites. The diffusion coefficient decays exponentially with decreasing T . Hence, the process of cooling the crystal from a certain temperature (probably much higher than room temperature) loses its quasi-static character. With further decrease in the temperature the crystal is frozen in a state with a small finite disorder.

All the atoms in the a sites are outside the first or second coordination of the empty b site. Therefore, each atom in the a site supplies two electrons to four of its neighbouring 7Y atoms (superfluous electrons for the multicentre bond). This leads to generation of a complex bivalent donor. In turn, four of the 5Y atoms neighbouring an empty b site have a deficit of two electrons to complete the multicentre bonds in the units around each 5Y atom. This results in a complex bivalent acceptor. In M_3V_2 compounds there exist other ways of

generating acceptor centres (interstitial Y atoms and non-stoichiometric vacancy of M atoms [3, 11]). Therefore the numbers of donors and acceptors are not equivalent. If the proposed influence of the remanent disorder is predominant, it leads to a p-type semiconductor (as are Zn_2As_2 and ZMA) with a high degree K of compensation. Therefore, interesting information about the remanent disorder may be obtained from study of the impurity conduction.

Transition to hopping conductivity with a constant activation energy E_a in Zn_3As_2 was established in [12]. In our previous work [13] it was found in ZMA at $T \approx 10$ K. In this section we investigate the influence of the remanent disorder on $E_a(x)$ by using the description given above for the disorder and generation of the impurity centres.

According to [14], we have, in conditions of high compensation, $E_a \approx [N_A/(1-K)]^{1/3}$ where $K = N_D/N_A$, and N_A and N_D are the concentrations of donors and acceptors, respectively. According to the mechanism described above, $N_A(x) = N_b[n_1(x) + n_2(x)]$, $1 - K(x) = [1 - K(0)]N_A(0)/N_A(x)$ and, hence,

$$E_a(x) = E_a(0)\{[n_1(x) + n_2(x)]/n_1(0)\}^{2/3}. \quad (14)$$

The concentrations of the remanent Zn and Mn atoms at the a sites can be obtained from low-temperature asymptotics of equations (8) as

$$n_1(x)/n_1(0) = (1-x)f^{1/2}(\alpha, \beta, x)F^{-1/2}(\alpha, x) \quad (15)$$

$$n_2(x)/n_1(0) = xf^{1/2}(\alpha, \beta, x)\exp(\alpha)F^{-1/2}(\alpha, x) \quad (16)$$

where $f(\alpha, \beta, x) = \exp[\alpha(41 - 35\beta)x]$, $F(\alpha, x) = 1 + x(\exp \alpha - 1)$, and $\alpha = 2[7(6 - 5\beta)]^{-1} \log[3^{1/2}n_1(0)](g - 1)$. The values of $E_a(x)$ determined from experimental data are shown in figure 6. The fit with equation (14) gives the parameters $\alpha = 9.0$ and $\beta = 1.19$. To find the value of g , we take $N_A(0) = N_b n_1(0) = (0.5-5.0) \times 10^{18} \text{ cm}^{-3}$. In conditions of high compensation this interval corresponds approximately to the concentration of holes in the exhaustion region $p_{ex} = 2N_A(1-K) \approx (1-7) \times 10^{17} \text{ cm}^{-3}$, as determined by Hall measurements at room temperature for undoped Zn_3As_2 crystals [3, 5]. Note that $N_A(0)$ is not a strictly determined parameter because the remanent disorder varies randomly from sample to sample. However, this uncertainty does not influence strongly our calculations because α has a logarithmic dependence on $n_1(0)$. As a result, we obtain $g = 0.61-0.70$.

The functions $n_1(x)$ and $n_2(x)$ calculated with equations (15) and (16) are shown in figure 7. Even at a low x all remanent disorder in ZMA is determined by the remanent concentration of Mn atoms at a sites.

Table 1. Data on the activation energy of hopping conductivity and on the Mn concentration at the a sites of ZMA for 'fresh' and 'old' crystals: E_a and n respective values for 'fresh' crystals; E_a^* and n_2^* , respective values for 'old' crystals.

x	E_a (meV)	E_a^* (meV)	E_a^*/E_a	n_2^*/n_2
0.00	0.11	0.11	1.00	—
0.02	0.45	0.31	0.69	0.57
0.10	0.92	0.56	0.61	0.48
0.13	0.90	0.37	0.41	0.26

The experimental data on E_a presented in figure 6 have been obtained from measurements of freshly grown crystals. It is interesting to compare the results with those obtained on the same crystals after storage for several years at room temperature as collected in table 1 (data with an asterisk). A systematic decrease in the activation energy and the remanent concentration of Mn at the a sites (calculated according to equation (14)) is evident.

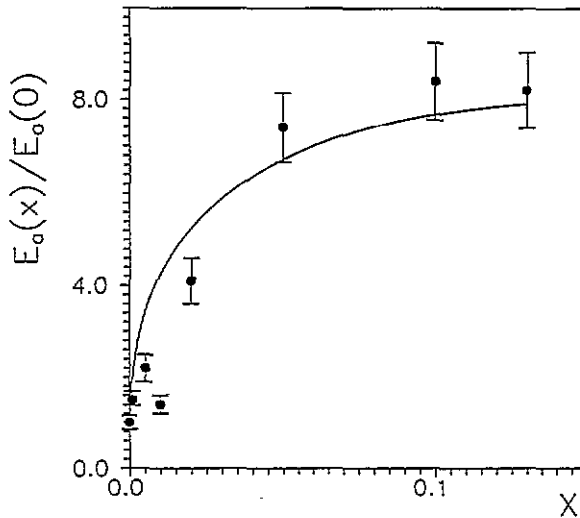


Figure 6. Experimental (●) and calculated (—) dependences of the activation energies E_a of hopping conductivity of ZMA on x .

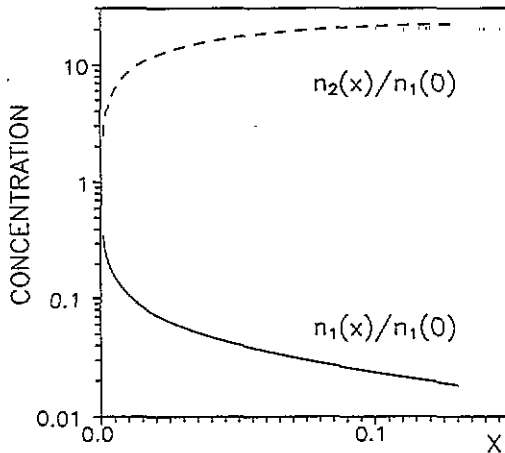


Figure 7. Remanent concentrations of Zn and Mn atoms versus x for ZMA.

The changes are higher for large values of x and demonstrate the relaxation of the crystals towards an equilibrium state.

4. Remanent disorder of vacant sites and magnetic properties of ZMA

4.1. Model of interacting clusters of polarization

For convenience the Mn atoms at the a and b sites are denoted below as A and B atoms, respectively. In order to make a transition between two nearest VSs the A atom should pass through a gap of $d - 2r_{As} \approx 2.9 \text{ \AA}$ where $d \approx 2^{1/2} \times 3 \text{ \AA}$ is the distance between two intermediate As atoms [7] and $r_{As} \approx 1.18 \text{ \AA}$ is the atomic covalent radius of As. The width of the gap exceeds twice the value of the Mn ionic radius ($r_{Mn} \approx 0.8 \text{ \AA}$). Therefore, the fact that the crystal structure of ZMA is isomorphic to Cd_3As_2 [7] provides sufficient freedom

for diffusion of the A atoms over VSs without replacement of other atoms in the lattice. As concluded in section 3, such diffusion is probably responsible for the slow relaxation of ZMA crystals with frozen-in remanent disorder towards an equilibrium ordered state.

We can write the activation energy of diffusion as $E_d = E_f - E_i$, where $E_i = 4E_7^{(2)}$ is the energy of the Mn atom in the initial state and $E_f = 4(p_5E_6^{(2)} + p_6E_7^{(2)} + p_7E_8^{(2)})$ is the energy of the diffusing atom in the final state, in two nearest VSs. In the initial state the diffusing atom in an overwhelming majority of cases is a seventh (superfluous) atom for each of its four neighbouring As atoms. In the final state it can be from fifth to seventh atom with probabilities between p_5 and p_7 , respectively. The values of the energies are $E_7^{(2)} = 6E_6^{(2)}/7$, $E_8^{(2)} = 6E_6^{(2)}/8$ and $E_6^{(2)} \approx 0.8$ eV which is the Mn-As interaction energy in the ideal sixfold As coordination (see sections 2.1 and 2.2). Considering the long-range order parameter s such that $1-s \approx 4 \times 10^{-3}$ we can write $p_5 = 5(1-s)/4$, $p_7 = 7(1-s)/4$ and $E_d = 21E_6^{(2)}(1-s)/2 \approx 40$ meV. This estimation is done for $T \approx T_{ph}$ but is valid also for $T \ll T_{ph}$ if the diffusing atoms are of the A type.

During the diffusion over VSs the A atom must come close to the Mn atoms on regular sites (i.e. B atoms), making a strong antiferromagnetic interaction with them. If $\tau_v \ll \tau_s$ (where τ_v is the time of transition between nearest VSs and τ_s is the spin relaxation time), a large number of spins belonging to B atoms would be partially polarized antiparallel to the A atom spin and weakly connected with each other within a volume $V_{cp} = 4\pi l_{cp}^3/3$ where $l_{cp} = (D\tau_s)^{1/2}$ is the diffusion length and $D = D_0 \exp(-E_d/kT)$ is the diffusion coefficient. We call such a structure a *cluster of polarization* (CP). The CP moment $M_{cp} = \beta_p g \mu_B S N_B V_{cp}$, where μ_B is the Bohr magneton, $g \approx 2$, $S = 5/2$, $N_B = N_x$ (N is the concentration of metallic atoms) and $\beta_p \approx 1$ is the degree of polarization, should be sufficiently high.

Supposing that $l_{cp} \ll l_A$ where $l_A = (4\pi N_A/3)^{-1/3}$ is the mean distance between CPs (N_A is the concentration of A atoms), the interaction between CPs can be treated in the dipole approximation. To obtain the conditions of freezing-in of the system of interacting CPs in the SG phase, we must find the region of non-zero solutions of the Edwards-Anderson parameter q [15, 16], defined for the CP moment, in the absence of the external magnetic field. The energy of the dipole interaction between the i th and j th CPs may be written as $H_{ij} = J_{ij} S_i \cdot S_j$. Here S_k is the classical spin of the CP and J_{ij} are coefficients depending on the orientation of the spins S_i and S_j and the vector distance R_{ij} between CPs. Since the distribution of CPs is random, we get the configurational averages $\langle J_{ij} \rangle \approx 0$, $\langle J_{ij}^2 \rangle^{1/2} \approx \alpha \gamma^2 / \langle R_{ij} \rangle^3$, and $\langle R_{ij} \rangle^3 \approx (4\pi N_A/3)^{-1}$ where $\gamma = \beta_p g \mu_B V_{cp} N_B$ and $\alpha \approx 1$ is a dimensionless coefficient. Using these relations the equation for q can be written in accordance with [15, 16] as

$$q = (2\pi)^{-1} \int dy \exp(-y^2/2) m^2 (2y I_0^{1/2} q^{1/2} / kT) \quad (17)$$

where $m(\xi) = M_{cp} L(\xi) / \mu_B$ is the magnetization, $L(\xi)$ is the Langevin function for $\xi = M_{cp} H / (kT)$, $I_0^{1/2} \approx (4/3) \pi \alpha z^{1/2} N_A M_{pc}^2 / S^2$ and $z \approx 6$ is the number of the nearest neighbours in the CP system. Using equation (17) the condition for existence $q \neq 0$ in zero field can be expressed as

$$kT \leq (2/3) (M_{cp} / \mu_B) I_0^{1/2}. \quad (18)$$

This inequality limits the temperature and the compositions where the CP moments can form a SG phase.

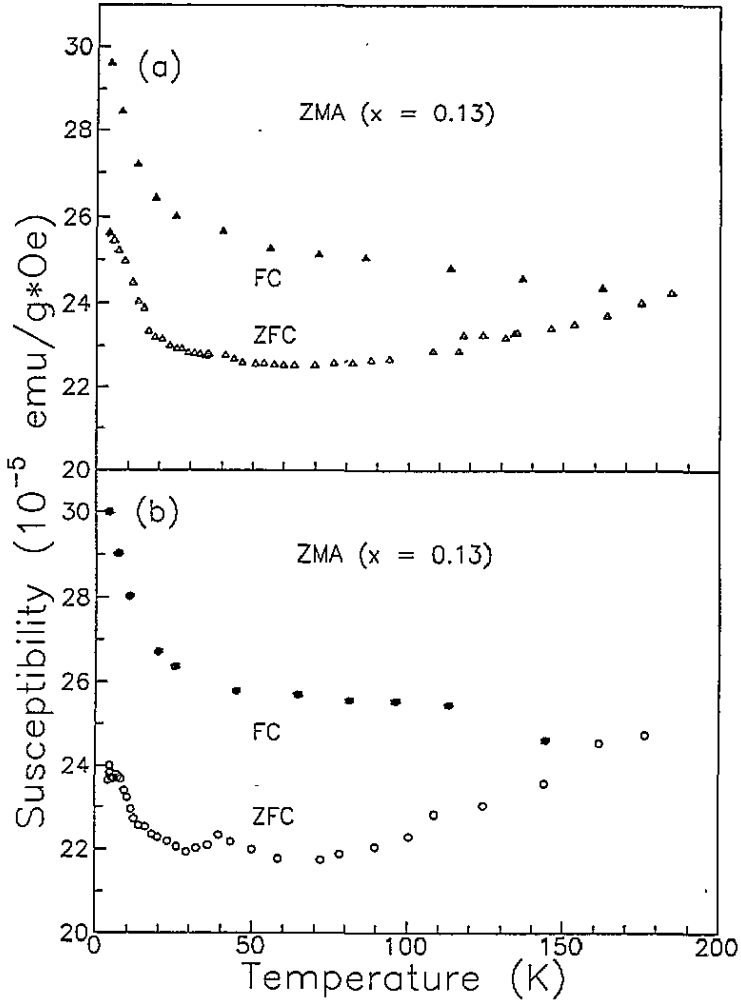


Figure 8. Zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities of ZMA with $x = 0.13$ versus temperature in fields of (a) 5 Oe and (b) 2 Oe [1].

4.2. Application to low-field magnetic measurements

The results of the magnetic susceptibility measurements on ZMA with $x = 0.13$ can be seen in figure 8 [1]. In addition to the spin-freezing effect around 200 K, several other magnetic anomalies can be observed:

- (i) low-temperature paramagnetic 'tails' at $T < 50$ K on both $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ (zero-field-cooled and field-cooled susceptibilities, respectively),
- (ii) a weak additional maximum at $T \approx 50$ K in $\chi_{ZFC}(T)$ observable at the lowest applied fields and
- (iii) a comparatively low value of $H_c \approx 600$ Oe above which all differences between $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ vanish and the magnetic susceptibility obeys the Curie-Weiss law [1].

All these anomalies have been observed also in another II_3V_2 diluted magnetic semiconductor $(\text{Cd}_{1-x}\text{Mn}_x)_3\text{As}_2$ (CMA) in the same intervals of composition ($x \geq 0.04$ –

0.05) and temperature [17]. The value of $H_c \approx 350$ Oe [17] is even lower for CMA.

The freezing temperature T_f can be estimated from equation (18) as $kT_f \approx n_{cp}E_{int}$, where n_{cp} is the mean number of B atom spins in a CP and $E_{int} \approx M_{cp}^2/l_A^3$ is the energy of interaction between CPs. The usual values of the dipole interaction energy lie within the approximate interval $1-10^{-2}$ meV [18]. Therefore, the requirement of a high $T_f \approx 10^2$ K [1, 17] is equivalent to $n_{cp} \approx 10-10^3$. This means that the conservation of the SG phase up to a high temperature must be connected with a large amount of *internal* spin degrees of freedom in the CP. On the other hand, the external magnetic field influences the *external* degrees of freedom (i.e. the total CP moment). The comparatively low values of H_c can be attributed to the small interaction (E_{int}) between CPs.

Using the condition (18), it is possible to explain other peculiarities of the susceptibility of ZMA mentioned above. Since $M_{cp} \approx (D\tau_s)^{3/2}$, it vanishes both at $T \rightarrow \infty$ (because $\tau_s \rightarrow 0$) and at $T \rightarrow 0$ (because $D \rightarrow 0$). Also, the value of M_{cp} is positive and is limited by saturation (completely polarized B atom spins within the volume V_{cp}). Therefore, the function $M_{cp}(T)$, as well as the right-hand side of the inequality (18), must have at least one maximum. This leads to a situation when solutions of the inequality (18) exist only at $x > x_c$ and within a limited interval $[T_2, T_1]$ (figure 9). The (T, x) -phase diagram looks like a horseshoe (figure 10), where the internal part (between the branches) corresponds to the SG phase, and the external part to the paramagnetic (PM) phase. Hence, the presence of the low-temperature PM tails on $\chi(T)$ (see figure 8) means a destruction of the SG phase caused by freezing-in of the diffusion of the A atoms.

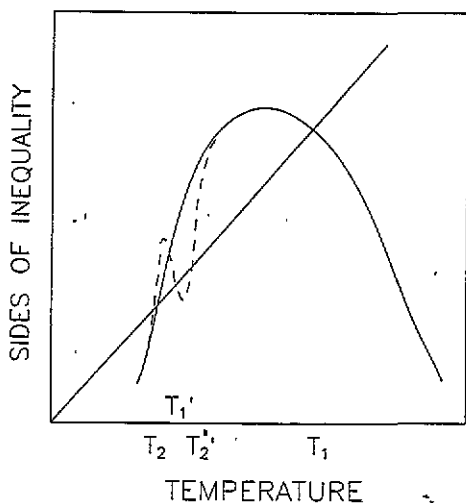


Figure 9. Schematic representation of the inequality (2). The straight line and the solid curve represent the left- and right-hand sides respectively, of the inequality. The broken curve is connected with the case of an additional maximum on the right-hand side as described in the text.

The character of the spin-lattice interaction varies when the temperature interval is changed [19, 20]. This may lead to the appearance of an additional maximum in $M_{cp}(T)$ (and the right-hand side of inequality (18)) near T_2 (see figure 9). This results in a paramagnetic 'window' (T_1', T_2') inside or near the SG interval $[T_2, T_1]$, where inequality (18) has no solution (see figure 9). Such a situation correlates with the presence of a weak maximum in $\chi_{ZFC}(T)$ of ZMA with $x = 0.08$ and 0.13 [1] and of CMA with $x = 0.10$ [17], observable at the lowest applied fields at $T \approx 50$ K (see, e.g., figure 8).

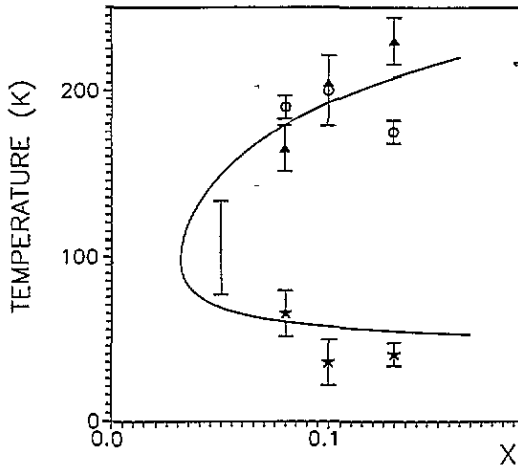


Figure 10. Comparison of the experimental and calculated (T, x) -phase diagrams. Values of T_1 (○) are determined from the position of the maximum of $\chi_{ZFC}(T)$, those of T_1 (△) are determined from the position of the maximum of $\chi_{ac}(T)$ and values of T_2 (★) are obtained from the end points of the PM tail on $\chi_{ZFC}(T)$. The error bar without a symbol corresponds to the sample with $x = 0.05$ [1]. The solid line gives the fit of equation (3) to the experimental data.

The spin-lattice interaction is characterized also with the PM relaxation time $\tau_{SL}(T)$ which can be approximated by a simple power law [19,20]. The exponent of this law is determined by the mechanism of the interaction and the temperature interval used and may vary within a wide range [19,20]. We assume the simplest law $\tau_s(T) \sim T^{-n}$ with n independent of T to be valid in ZMA over the temperature region considered below. This simplification corresponds to the single-maximum curve (see figure 9). Then all solutions of the inequality (18) lie between the roots of the equation

$$T = R_n [x^3 n_2(x)/n_1(0)]^{2/(2+9n)} \exp[-9/(2+9n)E_d/(kT)] \quad (19)$$

where

$$R_n = C_n \{(\mu_B^2 N/k)^2 N^6 [D_0 \tau_s(\Theta)]^9 \Theta^{9n}\}^{1/(2+9n)} \quad (20)$$

is a constant with the dimension of temperature, $\Theta = 275$ K is the Debye temperature of Zn_3As_2 [21] and

$$C_n = [(2/3)(4\pi/3)^4 6^{1/2} S \alpha \beta_p^3 g^3 n_1(0)]^{2/(2+9n)} \quad (21)$$

is a numerical constant. In these formulae we have used the relation $N_A = N n_2(x)$. The ratio $n_2(x)/n_1(0)$ has been found in section 3 and the value of $n_1(0)$ is between approximately 2×10^{-5} and 2×10^{-4} (see section 3).

The (T, x) -phase diagram is calculated using equation (19) and the solutions have been fitted with experimental data (see figure 10). The best fit is found with the values of $R_n = 385$ K and $n = 4.5$. Using these data, the values of some parameters of an arbitrary CP and characteristic energies were determined at $x = 0.1$ and $T = 200$ K. In these estimations we take $\alpha = 1$, $\beta_p = 1$ and $n_1(0) = 1 \times 10^{-4}$. As can be seen from equation (21), the uncertainty in these parameters does not influence the results strongly. Thus we obtain $l_{cp} \approx 10$ Å, $M_{cp} \approx 90\mu_B$, $E_{int} \approx 0.1$ meV and $E_c = M_{cp} H_c \approx 0.3$ meV.

Assuming that $D \approx v_T l$ at $T = T_{ph}$, where v_T is the thermal velocity of the diffusing atoms and $l \approx 3$ Å is the mean distance between the nearest sites in the lattice [7] we get $D_0 \approx 3 \times 10^{-3}$ cm² s⁻¹ and $\tau_s \approx 4 \times 10^{-11}$ s. The value of τ_v , estimated from the relation

$(E_f - E_i)\tau_v \geq 2\pi\hbar$, is $\tau_v \geq 10^{-13}$ s. Hence the values obtained for τ_v and τ_s do not contradict the condition $\tau_v \ll \tau_s$ suggested above.

5. Summary and conclusions

The problem of disorder in the stacking of VSs in the crystal structure of the II_3V_2 compounds and ZMA alloys has been investigated. We have obtained the values of the interaction energy in a metal–non-metal pair depending on the coordination of the non-metal atom in these materials. Two different effects (the order–disorder transition and the hopping conductivity) observed in two quite different temperature regions have been analysed. Both of them reveal some increase in the metal–non-metal interaction in a pair with a reduced coordination of the non-metal atom ($\beta < 1$), as well as the reduced energy of Mn–As interaction compared with that of Zn–As ($g < 1$). The values of the parameters β and g obtained independently from these effects (cf. sections 2 and 3, respectively) are in good agreement with each other. It was shown also that the Mn atoms at VSs play the main role in the disorder. Comparison of the data obtained on freshly grown crystals and on the same crystals after long storage at room temperature shows a slow relaxation of the non-equilibrium systems with a small frozen-in remanent disorder towards an equilibrium state.

Mn atoms in ZMA form two inequivalent subsystems: the atoms at the ‘regular’ sites and a comparatively small amount (about 2–5% at $x = 0.1$) of atoms in the VSs. The latter influence strongly the low-temperature conductivity of the alloys.

Using the concept of CPs (see section 4.1) it is possible to explain qualitatively all magnetic anomalies observed below $T_f \approx 200$ K in ZMA [1] and in CMA [3] in weak magnetic fields. The calculated (T, x) -phase diagram agrees well with the experimental susceptibility data, and the values of the CP parameters and characteristic energies obtained for ZMA are reasonable. This gives strong support to the formation of CPs with large magnetic moments and weak mutual interaction. The influence of the temperature and an external magnetic field is connected with the excitation of internal and external degrees of freedom respectively, in the CP. That is why the value of H_c above which the SG-like behaviour vanishes is comparatively low, whereas the spin-freezing temperature is very high.

On the other hand, the dipole approximation appears rather rough ($l_A \approx 15\text{--}20$ Å at $x \approx 0.1$), the law $\tau_s \sim T^{-n}$ is obviously simplified, and the values of the diffusion parameters are only estimates. Therefore, in particular, there is strong need for detailed experimental investigations into spin relaxation and diffusion processes in ZMA. Also more accurate values of τ_v should be obtained.

Additional verification of our model would be obtained by magnetic and galvanomagnetic measurements on crystals with controlled remanent disorder. Such crystals may be obtained by annealing, by vapour-phase growth or by long storage at room temperature.

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