Journal of Magnetism and Magnetic Materials 140–144 (1995) 2019–2020

ELSEVIER

Journal of magnetism and magnetic materials

Vacancy-type disorder in $(Zn_{1-x}Mn_x)_3As_2$

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Abstract

Disorder in stacking of vacant cites in the crystal structure of the diluted magnetic semiconducting alloy $(Zn_{1-x}Mn_x)_3As_2$ is studied. Compositional dependencies of the order–disorder transition temperature, and the activation energy of hopping conductivity are analyzed, paying attention to atoms in the sites which are vacant in a completely ordered state.

The alloys $(Zn_{1-x}Mn_x)_3As_2$, briefly ZMA, belong to the new class of diluted magnetic semiconductors based on the II_3V_2-type compounds. Single crystals of these alloys demonstrate interesting magnetic properties, including two spin-freezing effects observed at quite different temperatures, $T < 4$ K [1], and $T \sim 200$ K [2].

The crystal structure of II_3V_2 compounds, and ZMA, contains 1/4 part of vacant sites (VS) in the metallic sublattice. The stacking of VS has a long-range ordering at $T < T_{ph}$ and is completely disordered at $T > T_{ph}$ [3] (T_{ph} is a temperature of the order–disorder transition). The problems studied in the present paper, are connected with this transition and the remanent disorder of VS in ZMA at $T \ll T_{ph}$.

Our description of the disorder in ZMA is based on the Bragg–Williams approximation and a pair approximation of the multicenter covalent bonds characteristic to II_3V_2 compounds [4]. The deviation from the long-range ordering of VS leads to appearance of As atoms whose metallic coordination, k, differs from the ideal sixfold one. Therefore the energy of the metal–non-metal interaction, $E_k^{(i)}$, depends on k. Here $i = 1, 2$ with the index 1 attributed always to Zn atoms, and the index 2 to Mn atoms. If n_1, n_2 are the concentrations of the metallic atoms (in units of the concentration of Zn in Zn_3As_2) then a pair of equations can be obtained by minimizing the free energy of the crystal [5]:

$$\log\left\{3n_i(n_i+n_j)/\left[(\xi_i-n_i)(1-3n_i-3n_j)\right]\right\} = -w_i/\tau, \quad (1)$$

where $\xi_1 = 1-x$, $\xi_2 = x$, $\tau = kT\,|\,E_6^{(1)}\,|^{-1}$ and w_i is the energy of disordering of VS by ith type of atoms. The energies w_i are some functions of x, n_1, n_2, which depend on n_i as polynomials of 7th power. The long-range order parameter can be written as $S = 1 - 4(n_1 + n_2)$.

There exist untrivial solutions of Eq. (1) up to $T = T_{ph}$, at which a first-order phase transition occurs. The leap of S takes place from a completely disordered state, $S = 0$, to an almost ordered state with $1 - S \approx 4 \times 10^{-4}$. If the condition $g = E_6^{(2)}/E_6^{(1)} < 1$ is fulfilled, the temperature of the transition in ZMA is shifted to lower values. This agrees with the experimental results (see Fig. 1). The best fit with the experimental data is obtained with the values of $g = 0.64$, $\beta = 1.16$. Here $\beta = E_L^{(i)}/E_6^{(i)}$, and $E_L^{(i)}$ is the energy of metal–non-metal interaction when $k < 6$. The value of β is constant, because it depends only on the crystal structure which is isomorphic for ZMA and Zn_3As_2.

The remanent disorder of VS in ZMA is connected with deviation from the quasi-static character of cooling

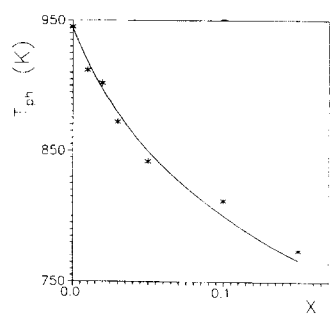

Fig. 1. Dependence of the transition temperature T_{ph}, determined by X-ray measurements, on composition in ZMA. The experimental values are denoted with (*). The solid line gives the theoretical values. The measured data of T_{ph} are accurate to within ±1%.

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SSDI 0304-8853(94)01205-9

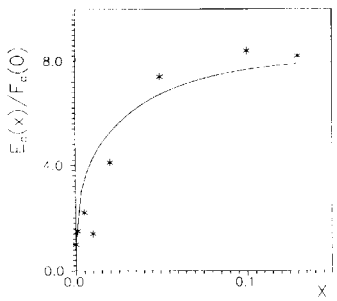

Fig. 2. Comparison of the experimental (*) compositional dependence of the activation energy of hopping conductivity in ZMA with that calculated from Eq. (2) (solid line).

the samples. At temperatures $T \ll T_{ph}$ such crystal can be treated as a system with a small frozen-in disorder. A slow relaxation to the equilibrium, or the ordered state, takes place due to diffusion of atoms over VS towards the nearest empty regular cites. Such disorder leads to generation of impurity centers. Therefore it exerts strong influence to the activation energy, E_a, of the hopping conductivity observed in ZMA below $T \sim 10$ K [6]. In conditions of a high degree of compensation [7], we can write

$$E_a(x) = E_a(0) \cdot \{[n_1(x) + n_2(x)]/n_1(0)\}^{2/3}, \qquad (2)$$

where the functions $n_i(x)$ are obtained by taking the low-temperature asymptotics of Eq. (1). The best agreement with the experimental results (Fig. 2) is achieved with values of $\beta = 1.19$, and $g = 0.70$–0.61. Some uncertainty of g is connected with the corresponding uncertainty of $n_1(0)$, which is not a strictly determined parameter. The ratios $n_1(x)/n_1(0)$ and $n_2(x)/n_1(0)$ appearing in Eq. (2) are shown in Fig. 3. Even at low x all remanent disorder in ZMA is determined by Mn atoms in VS.

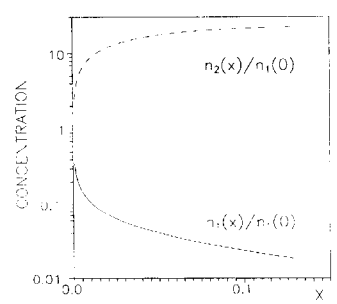

Fig. 3. Compositional dependence of the remanent concentrations of Zn and Mn atoms in vacant cites.

Table 1
Comparison of data obtained on 'fresh' and '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

A slow relaxation of the crystals towards an ordered equilibrium state is obvious from the data collected in Table 1. This table presents the parameters obtained for freshly grown crystals and for the same crystals after several years of storage at room temperature (data are marked by *).

We conclude that the independent analysis of the two different effects taking place at two quite different temperature regions (Figs. 1 and 2) gives very close values of the pair of parameters g and β. Mn in ZMA forms two inequivalent systems, including the atoms in the regular cites, and some amount (about 2–5% at $x = 0.1$) of atoms in the sites which are vacant in a completely ordered state. The relaxation of the crystals with frozen-in disorder towards the equilibrium state (Table 1) is more pronounced in the samples with higher Mn concentration. It agrees well with the compositional dependence of the remanent Zn and Mn concentrations in VS (Fig. 2).

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