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Electronic band structure and magnetic susceptibility of $Ge_{1-x}Si_x$ solid solutions

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Abstract. The magnetic susceptibility (MS) of single crystal $Ge_{1-x}Si_x$ ($0 \le x \le 0.1$) solid solutions was investigated. Considerable anomalous MS behavior was found. Theoretical estimations of paramagnetic and diamagnetic parts were made. Reconstruction of the band structure of these alloys results in peculiarities of MS as a function of the composition.

Keywords: band structure, magnetic susceptibility, $Ge_{1-x}Si_x$, alloy.

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1. Introduction

The main consequence of alloying germanium with silicon is the reconstruction of the band structure of $Ge_{1-x}Si_x$ alloys (x is the molar fraction of Si) as a function of the Si concentration. When $x = 0.14$, minima of the conduction band of the types L_1 and Δ_1 are located at the same energy level, whereas, when $x > 0.14$, inversion of the conduction band of the type $L_1 \rightarrow \Delta_1$ occurs. The $Ge_{1-x}Si_x$ alloys are a siutable object for the purpose of studying galvanomagnetic properties of semiconductors with changing dispersion law.

Magnetic susceptibility (MS) of the alloys allows to receive reliable information about the nature of interatomic interaction and parameters of chemical bonding. The specificity of MS is that it does not depend on the scattering mechanisms, but it is formed by features of the electronic band structure. The doping Ge by silicon leads to the dynamics of electronic bands, therefore to the change in the topology of $E(\boldsymbol{k})$ over Brillouin zone and as a rule in concentration dependence of MS [1].

2. Experimental procedure

We investigated $Ge_{1-x}Si_x$, doped by Sb up to concentration 10^{14}–10^{15} cm^{-3}. The highest content of the minority component is 10 at. %. After X-ray microanalysis measurements, irregularity of Si distribution over the sample did not exceed 0.1%. The surface density of dislocations was 10^3 cm^{-2} and it increases due to increase of Si composition up to 10^6 cm^{-2}.

MS of $Ge_{1-x}Si_x$ alloys was investigated by the Faraday method within the temperature range 77–300 K and at the magnetic field 0.3–5 kOe. The samples with $1.5 \times 1.5 \times 10$ mm^3 dimensions were oriented along [100], [111], [110] directions. MS measurement error did not exceed 2%. In accuracy measurement limits the anisotropy of MS was not observed. MS was not temperature and magnetic field dependent. The experimental and theoretical results are presented in the table (χ_{expt} – the experimental MS at 77 K) and the Fig. 1.

3. Theoretical estimations

Magnetic susceptibility of semiconductors consists of Langevin's diamagnetic χ_L, Van Vleck's paramagnetic χ_P terms and also the defects contribution $\chi_d(T)$:

$$\chi = \chi_L + \chi_P + \chi_d(T) \qquad (1)$$

Hamiltonian of the electron system in the external magnetic field can be written as

$$H = \sum_k \frac{1}{2m}\left(\vec{p}_k - \frac{e}{c}\vec{A}_k\right)^2 + U + \sum_k \frac{e}{mc}\left(\vec{S}_k rot \vec{A}_k\right) \qquad (2)$$

where $\vec{p}_k$ and $\vec{S}_k$ are operators of momentum and spin respectively, $\vec{A}_k$ – vector-potential of external magnetic field,

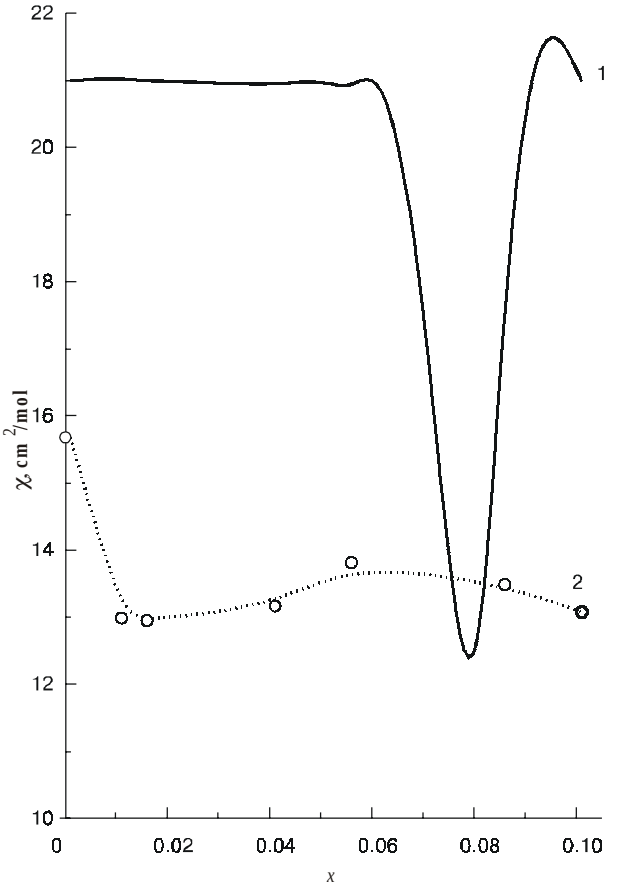

Fig. 1. Magnetic susceptibility variation $\chi(x)$ vs x for $Ge_{1-x}Si_x$ alloys (*1* – theory, *2* – experimental data at 77 K).

U – potential energy of electrostatic interaction of the electrons and the summation runs over all electronic states of the system. For the homogeneous magnetic field directed along OZ axis the expression (2) transforms into the following:

$$\hat{H} = \sum_k \left[-\frac{\hbar^2}{2m}\nabla_k^2 + H_z \frac{e\hbar}{2mci}\left(x_k \frac{\partial}{\partial y_k} - y_k \frac{\partial}{\partial x_k} \right) + \right.$$
$$\left. + H_z^2 \frac{e^2}{8mc^2}\left(x_k^2 + y_k^2\right)\right] + U + \sum_k \frac{e}{mc} H_z S_k \qquad (3)$$

The multiplier $\frac{e}{2mc} H_z$ in the second summand within square brackets is the operator of z-component of angular momentum.

$$l_{zk} = \frac{\hbar}{i}\left(x_k \frac{\partial}{\partial y_k} - y_k \frac{\partial}{\partial x_k} \right) \qquad (4)$$

Than the terms in (3), that linear depend on H_z, are:

$$-H \frac{|e|}{2mc} \sum_k \left(l_{zk} + 2S_{zk} \right) = -H_z M_z \qquad (5)$$

M_z is the operator of full electronic momentum. MS can be defined as:

$$\chi = -\frac{\partial^2 E}{\partial H_z^2} = -\frac{\partial^2 \left\langle n \middle| \hat{H} \middle| n \right\rangle}{\partial H_z^2} \qquad (6)$$

For the calculation of (6), we used the perturbation theory, supposing that the perturbation is interaction with magnetic field. Than

$$H = H_o + H_z W^{(1)} + H_z^2 W^{(2)} + \ldots = H_o + H_1 \qquad (7)$$

$$H_1 = -H_z M_z + H_z^2 \frac{e^2}{8mc^2}\left(x_k^2 + y_k^2\right) \qquad (8)$$

The energy of this system, taking into account the second order terms over H_z, is equal]

$$\varepsilon_n = \varepsilon_n^o - H_z \left\langle n \middle| M_z^o \middle| n \right\rangle + H_z^2 \frac{e^2}{8mc^2} \sum_k \left\langle n \middle| \left(x_k^2 + y_k^2 \right) \middle| n \right\rangle -$$
$$- H_z^2 \sum_{n'} \frac{\left| n \middle\langle M_z^o \middle\rangle n' \right|^2}{\varepsilon_{n'}^{(o)} - \varepsilon_n^{(o)}} \qquad (9)$$

Substituting (9) into (6), the second term in energy gives Langevin diamagnetic susceptibility and the third term is Van Vleck paramagnetic susceptibility. In the case of tetrahedral covalent semiconductors, Langevin diamagnetic susceptibility is:

$$\chi_L = -\frac{\gamma_m^2 N e^2 d^2}{24mc^2} \qquad (10)$$

where d is the bond length, N – electronic density, γ_m – scaling factor, that equal 1.12 for all semiconductors.

The paramagnetic contribution to MS can be presented [3]:

$$\chi_p = \frac{2\mu_B^2}{(2\pi)^3} \times$$
$$\times \sum_n^{occ} \sum_{n'} P \int d\vec{k} \frac{\left| M^{nn'}(\vec{k}) \right|^2 f\left(E_n(\vec{k})\right)\left[1 - f\left(E_{n'}(\vec{k})\right)\right]}{E_{n'}(\vec{k}) - E_n(\vec{k})} \qquad (11)$$

where $E_n(\vec{k})$ is the energy of n-th band at $\vec{k}$ point of Brillouin zone (BZ); $M^{nn'}$ – the oscillator strength; f – Fermi-Dirac distribution function; P – means principal value integration.

For the determination of Ge and Si band structure $E_n(\vec{k})$, we used the tight-binding method [2]. As basic functions we chose *s*-, p_x-, p_y-, p_z- and *s**- orbitals of anions and cations, than the secular equation can be solved in nearest neighbors approximation. We fit band structure in the high symmetrical points of Brillouin zone to the most

recent experimental data. The two-center approximation is used for expressions of interatomic matrix elements and only nearest-neighbor interactions are taken into account. In our investigations of the $Ge_{1-x}Si_x$ solid solution band structure, we calculate the parameters of interactions in virtual crystal approximation (VCA). Integral (11) over Brillouin zone was calculated using thelinear tetrahedron method [4]. In this method the 1/48-th part of BZ is divided by 256 identical tetrahedrons.

Paramagnetic part of MS (11) was calculated at T = = 0 K. We supposed also that the matrix elements of the oscillator strength are constant within the tetrahedron that corresponds to the Lehmann-Taut division. Than if we expand the energy difference into the Taylor series up to the first order with respect to $(\vec{k}-\vec{k}_o)$ at the $\vec{k}_o$ point, we obtain the following integrals

$$I_{nn'} = P\int \frac{d^3\vec{k}}{A+\vec{B}(\vec{k}-\vec{k}_o)} \tag{12}$$

where

$$A = E_{n'}(\vec{k}) - E_n(\vec{k}) \tag{13}$$

$$\vec{B} = \vec{\nabla}_k\left[E_{n'}(\vec{k}) - E_n(\vec{k})\right] \tag{14}$$

at $\vec{k} = \vec{k}_o$. Since the tetrahedrons have equal volumes, than the integral (11) can be expressed analytically as [3]:

$$I_{nn'} = 3\Omega\left(\frac{v_1^2}{D_1}\ln\left|\frac{v_1}{v_4}\right| + \frac{v_2^2}{D_2}\ln\left|\frac{v_2}{v_4}\right| + \frac{v_3^2}{D_3}\ln\left|\frac{v_3}{v_4}\right|\right) \tag{15}$$

where Ω is a tetrahedron volume, $v_i = E_{n'}(\vec{k}_i) - E_n(\vec{k}_i)$. Index i means the four tetrahedron apexes in which the energies are defined. Besides that

$$\begin{aligned} D_1 &= (v_1-v_4)(v_1-v_3)(v_1-v_2)\\ D_2 &= (v_2-v_4)(v_2-v_3)(v_2-v_1)\\ D_3 &= (v_3-v_4)(v_3-v_2)(v_3-v_1) \end{aligned} \tag{16}$$

Paramagnetic susceptibility can be expressed in terms of integrals $I_{nn'}$ introduced above

$$\chi_p = \frac{2\mu_B^2}{(2\pi)^3}\sum_n^{occ}\sum_{n'}\left|M^{nn'}\right|^2 I_{nn'} \tag{17}$$

For the $Ge_{1-x}Si_x$ alloys the composition dependence of MS is defined by the reconstruction of the electronic band structure.

Matrix elements of the oscillator strength in the tight-binding method can be estimated following Harrison [2]:

$$\left|M_{nn'}\right|^2 \propto \frac{2\hbar^2}{m(E_{n'}-E_n)}\left|\langle n|\frac{\partial}{\partial x}|n'\rangle\right|^2 \tag{18}$$

From the quantum mechanical view, we can write

$$\langle n|\frac{\partial}{\partial x}|n'\rangle = \frac{m(E_{n'}-E_n)}{\hbar^2}\langle n|x|n'\rangle \tag{19}$$

On the other hand,

$$\langle n|x|n'\rangle = \frac{\gamma d}{2\sqrt{3}}(1-\alpha_p)^{1/2}$$

where γ is the scaling factor; α_p is the ionicity of the bond; $|n\rangle$, $|n'\rangle$ and $E_{n'}$, E_n are the eigenfunctions and eigenvalues of the energy of antibonding and bonding states, respectively. Then using (19), (20) and (18) we obtain:

$$\left|M_{nn'}\right|^2 \propto \frac{2m(E_{n'}-E_n)}{\hbar^2}\left|\langle n|x|n'\rangle\right|^2 \sim 10^{-2} \tag{21}$$

Experimental (at 77 K) and theoretical results are presented in the Table. The diamagnetic and paramagnetic contributions to the MS were calculated using (10) and (17), respectively. As seen from the Table, the small changes of the alloy composition caused increasing of the paramagnetic part of MS. In figure we plot the total MS (1 – theory; 2 – experiment at 77 K).

As illustrated by the figure, the composition dependence of MS has some peculiarities. They are obviously connected with paramagnetic part of MS and caused by

Table. Comparison of the theoretical calculations on magnetic susceptibility with experimental data for $Ge_{1-x}Si_x$ (at 77 K).

x	$\chi\cdot10^6$, cm^3mol^{-1}			
	$-\chi_{expt}$	$-\chi_L$	χ_p	$-(\chi_L+\chi_p)$
0	15.68	21.123	0.11866	21
0.01	12.99	21.108	0.08569	21.02
0.015	12.95	—	—	—
0.02	—	21.09	0.1066	20.98
0.03	—	21.076	0.11126	20.96
0.04	13.17	21.06	0.1054	20.95
0.05	—	21.045	0.0868	20.96
0.055	13.82	—	—	—
0.06	—	21.03	0.10347	20.93
0.07	—	21.01	0.12038	20.89
0.08	—	20.99	0.89	12.9
0.085	13.49	—	—	—
0.09	—	20.98	0.092	20.88
0.1	13.08	20.967	0.0917	20.87

the changes in the topology of the electronic structure of alloys with increasing Si concentration in solid solutions. The difference between calculated and experimental positions of singularities is due to insufficient precision of the used version of the tight-binding method in calculations of $E_n(\bar{k})$, and also due to the linearity of integration over BZ. In our theoretical calculations, we did not take into account the impurity contribution to MS and influence of the temperature, too.

However, it follows from our experimental investigations [1] that the influence of the impurities and defects on MS is strong. Moreover, the distribution of silicon atoms in $Ge_{1-x}Si_x$ alloys is nonuniform. The scale of fluctuations of the composition (geometric dimensions 50–100 Å and number of silicon atoms per cluster 30–150) was estimated in [5]. The presence of these clusters causes the great local distortions of the crystal lattice and the changes of the electron density configuration.

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