the unit cell), T-192 (tetragonal, with 190-192 atoms per unit cell), and γ-boron (high pressure phase, orthorhombic, with 28 atoms per unit cell). The new phase turned out to be a key to understanding the phase diagram of boron-the only element for which the phase diagram was unknown since its discovery 200 years ago.

Here, we report the synthesis of γ- and T-192 boron from β-boron at pressures up to 18 GPa and temperatures up to 2200 °C using a multianvil apparatus combined with x-ray diffraction (XRD) and Raman spectra. Based on the XRD and Raman results, we give the phase boundary of β-, γ-, and T-192 boron. Fig.1 shows the phase relations between β-boron (open), γ-boron (solid) and T phase (inverse triangles) based on the results of the multianvil quenched experiments. The semi-solid circles represent β-boron and γ-boron in coexistence. The line is a phase boundary between β-boron and γ-boron, and the inset show the theoretical phase boundary from Oganov *et al.*[1] and the tentative phase boundary from Zarechnaya *et al.*[2]. Additionally, the two open inverse triangle represent P-T conditions of T-192 phase from Oganov *et al.*[1] and Ma *et al.*[3] respectively. Combined with the previous results [1], [2] and our study, γ-boron phase becomes stable under a certain pressures (above ~8.5 GPa), and β-boron can transform into γ-boron above ~8.5 GPa and using heating to overcome kinetic barriers, and the kinetic barriers decrease with increasing pressure. However, at higher temperatures, β-boron and T-192 phase are more stable than γ-boron, thus γ-boron transforms back to β-boron (~9 GPa) or continues to transform into T-192 phase (above ~10 GPa) with increasing temperature depend on undergoing high pressure.

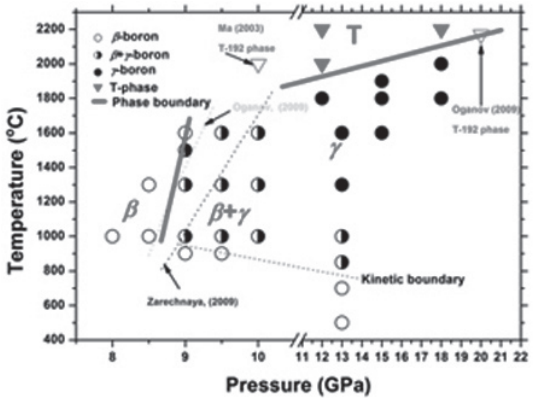

Fig.1 Phase relations between β-boron, γ-boron and T phase

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Keywords: boron, phase boundary, high pressure and high temperature

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Structural anomaly in a novel iron-based perovskite

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Recent discovery of iron-based perovskites $ACu_3Fe_4O_{12}$ (A = Ca and La) has been attracting much interest due to the fascinating and unexpected properties. A charge disproportionation (CD) of Fe^{4+} into Fe^{3+} and Fe^{5+} occurs in $CaCu_3Fe_4O_{12}$ (CCFO) [1], whereas an intersite charge transfer (CT) between Cu and Fe results in a large volume change in $LaCu_3Fe_4O_{12}$ [2]. The different electronic phases resulted from CD/CT imply that further anomalous properties can be achieved in this system.

A novel iron-based perovskite $SrCu_3Fe_4O_{12}$ (SCFO) was successfully synthesized using high-pressure of 15 GPa. The structural and physical properties of SCFO were in contrast to those of the known $ACu_3Fe_4O_{12}$ (A = Ca and La) perovskites. SCFO demonstrated a large negative thermal expansion (NTE) with a linear expansion coefficient (ca. $-2x10^{-5}$ K^{-1} at maximum) in a temperature range of 170–270 K. The Rietveld refinement based on the synchrotron X-ray powder diffraction data revealed that the NTE was attributed to a continuous intersite CT between Cu and Fe. Mössbauer spectroscopy exhibited that SCFO resulted in a charge disproportionated state below ~200 K. The relative abundance of Fe^{3+}: Fe^{5+} = 4: 1, which is different from the ratio of 1: 1 for CCFO, implies the electron doping into Fe through intersite charge transfer.

[1] I. Yamada et al., *Angew. Chem. Int. Ed.* **2008**, *47*, 7032–7035. [2] Y,W. Long et al., *Nature* **2009,** *458*, 60–63.

Keywords: novel perovskite, negative thermal expansion, high-pressure synthesis

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Electron and magnetic properties in high temperatures magnetic semiconductors at high pressure up to 7 GPa

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In high-temperature ferromagnetic semiconductors $Cd_{1-x}Mn_xGeAs$ (x=0÷0.36) and $Cd_{1-x}Mn_xGeP_2$ (x=0÷0.225) there is carried out a complex investigation of electric and magnetic properties. The baric dependences of the specific resistance ρ, Hall coefficient R_H, and relative magnetic susceptibility χ/χ_0 are measured. The ρ(P) and R(P) are measured in high-pressure device of "Toroid" type [1], [2] when pressure rises and falls up to 7 GPa. The magnetic susceptibility is estimated by a method described in the work [3]. Structural phase transitions are found in baric dependences of ρ(P) and R_H(P) in both compounds at increase and decrease in pressure. A position of phase transitions sifts towards the high pressures when a percentage of Mn increases. All phase transitions are reversible in $Cd_{1-x}Mn_xGeAs_2$, in $Cd_{1-x}Mn_xGeP_2$ samples with x≤0.135 the phase transition is accompanied by partial decomposition of a substance, what confirms the X-ray diffraction study before and after pressure applying on dependences (χ/χ_0)P. In all samples of both compounds there are observed the magnetic phase transitions which shift towards high pressures with increase in percentage of Mn. When pressure decreases the hysteresis emerges. A magnetic phase transition is not revealed in base samples of CdGeAs and CdGeP. We interpret the observed phase transitions as non-magnetic phase transition [4]. The temperature dependences of normal and abnormal Hall coefficients are calculated from magnetic-field dependences of Hall resistance for $Cd_{1-x}Mn_xGeAs_2$ (x=0÷0.36) by the method of interactive graphical plotting.

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[1] L.G. Khvostantsev, L.P. Vereshagin, A.P. Novikov. *High Temp.-High Pressure* **1977**, *9, 6,* 637-639. [2] A. Yu. Mollaev, R.K. Arslanov, L.A. Saypulaeva, S.F. Marenkin. *Inorganic materials* **2001**, *37, 4,* 405-408. [3] A. Yu. Mollaev, I.K. Kamilov, S.F. Marenkin, R.K. Arslanov, U.Z. Zalibekov, T.R. Arslanov, A.A. Abdullaev, I.V. Fedorchenko. *Inorganic materials* **2010**, *46, 9*, 927-931. [4] A. Yu. Mollaev, I.K. Kamilov, R.K. Arslanov, T.R. Arslanov, U.Z. Zalibekov, V.M. Novototzev, S.F. Marenkin. *Jetf Letters* **2010**, *91, 9*, 524-526.

Keywords: electric, magnetic, pressure

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Magnetovolume effect in diluted magnetic semiconductors $CdGeAs_2$:Mn and$CdGeP_2$:Mn at high pressure

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The given work presents the experimental results on relative volume compressibility $\Delta V(P)/V_0$ from the pressure P≤7 GPa at room temperatures in diluted magnetic semiconductors $Cd_{1-x}Mn_xGeAs_2$ (x=0÷0.36) and p-$Cd_{1-x}Mn_xGeP_2$ (x=0.09 ≤x≤ 0.225). The measurements are carried out in a high pressure device of toroid type at the hydrostatic pressure up to P≤7 GPa in region room temperatures. A detailed description of a method of the experiment is given in work [1]. The synthesis of the samples and technological modes of their growth are described in work [2].

Compressibility is measured by the tensometric technique as in [3]. The measured samples have a cylinder shape of 1mm in a height and 3 mm in a diameter.

An extinction of ferromagnetic state under the pressure in $Cd_{1-x}Mn_xGeAs_2$ (x=0÷0.36) reveals as a sharp decrease in lattice compressibility and increase in bulk modulus beginning from P>4.5 GPa. The bulk modulus rises in wide pressure ranges above 4.5 GPa and gradually increases close to 7GPa, what indicates that the magnetic transition "ferromagnetic-paramagnetic" occurred at this pressure.

The anomalies of magnetic properties are found on the $\Delta V(P)/V_0$ dependences in $Cd_{1-x}Mn_xGeP_2$ (x=0.09 ≤x≤ 0.225) at P>3.5. In our pinion the obtained results show that magnetic phase transitions take place in all studied samples. A transition from the magnetic-ordered phase into the magnetic-disordered phase occurs near a critical pressure P_c>3.5GPa. High pressures significantly decrease the Curie temperature (T_c) in all researched polycrystals. The values for volume magnetostriction (coefficient of spontaneous magnetization) are determined from the $\Delta V(P)/V_0$ dependences. The calculations of bulk modulus B carried out by means of scaling expression allow to estimate the values of bulk modulus in magnetic-ordered and magnetic-disordered phases.

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[1] L. G. Khvostantsev, L. P. Vereshagin, A. P. Novikov. *High Temp.-High Pressure* **1977**, 9, 6, 637-639. [2] S. F. Marenkin, V. M.Novotortzev, K. K. Palkina et al., *Inorganic materials* **2004**, 40, 2, 135-137. [3] O. B. Tsiok, V. V. Bredikhin, V. A. Sidorov and L. G. Khvostantsev, *High Pressure Res.* **1992**, 10, 523-533.

Keywords: Magnetic, Pressure, Tensometry

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Negative magnetoresistance in $CdGeP_2$:Mn induced by high pressure

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Three-component semiconductors of $A^{II}B^{IV}C^{V}_2$ group, in particular, $CdGeP_2$ on the base of which is firstly synthesized a high-temperature ferromagnetic [1], are conditioned by doping ability of diamond-like matrixes by transition elements (Mn, Fe, Cr, etc.) in rather wide intervals, high mobility of p-type carriers, high Currie temperatures. The baric dependences of negative magnetoresistance are measured in the polycrystalline samples of p-$Cd_{1-x}Mn_xGeP_2$ with (x=0.09 ≤x≤ 0.225) in a high pressure device of "Toroid" type at hydrostatic pressures up to P≤6GPa in a range of room temperatures, when pressure rises and falls. A detailed description of a method of the experiment is given in works [2].

In all studied samples of p-$Cd_{1-x}Mn_xGeP_2$ with (x=0.09 ≤x≤ 0.225) except the base CdGeP there is observed the transverse magnetoresistance induced by pressure, which is positive initially and becomes negative in a region of the magnetic phase transition (Fig. 1). Increase in pressure and magnetic field leads to rise magnetoresistance magnitude. The magnetic phase transitions are revealed in all samples of p-$Cd_{1-x}Mn_xGeP_2$ with (x=0.09 ≤x≤ 0.225) except the base $CdGeP_2$ at pressure rising. The experimental results on a behavior of impurities of transition metals allow assuming that Mn ions occupy the sites in Cd sublattice in CdGeP. The observed negative magnetoresistance confirms an interaction of carriers with magnetic moments of Mn ions. So we can conclude that a metamagnetic transition from low magnetization state to the high magnetization occurs in $Cd_{1-x}Mn_xGeP_2$ with (x=0.09 ≤x≤ 0.225) of chalcopyrite structure near the T_c.

This work was supported by Program of Presidium of RAS "Thermophysics and mechanics of external energetic influences and physics of high compressed material" and Section of High Compressed Material.

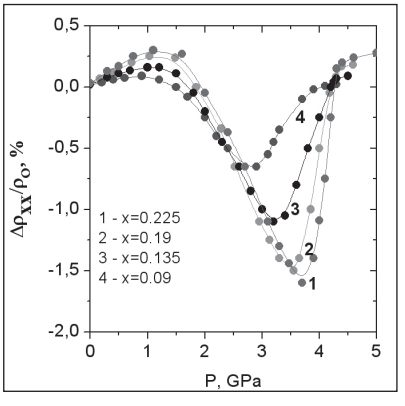

Fig.1. The baric dependence of transverse magnetoresistance ρ_{xx}/ρ_0 in a magnetic field H=5 kOe for $Cd_{1-x}Mn_xGeP_2$ with different level of Mn.