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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. Novotortzev, S.F. Marenkin. *Jetf Letters* **2010**, *91*, 9, 524-526.

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Magnetovolume effect in diluted magnetic semiconductors CdGeAs₂:Mn and CdGeP₂: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 $P \leq 7$ GPa at room temperatures in diluted magnetic semiconductors Cd_{1-x}Mn_xGeAs₂ ($x=0 \div 0.36$) and p-Cd_{1-x}Mn_xGeP₂ ($x=0.09 \leq x \leq 0.225$). The measurements are carried out in a high pressure device of toroid type at the hydrostatic pressure up to $P \leq 7$ 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 1 mm in a height and 3 mm in a diameter.

An extinction of ferromagnetic state under the pressure in Cd_{1-x}Mn_xGeAs₂ ($x=0 \div 0.36$) 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 7 GPa, 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_xGeP₂ ($x=0.09 \leq x \leq 0.225$) 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 $P_c > 3.5$ GPa. 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.

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Negative magnetoresistance in CdGeP₂:Mn induced by high pressure

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Three-component semiconductors of A^{II}B^{IV}C^V₂ group, in particular, CdGeP₂ 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_xGeP₂ with ($x=0.09 \leq x \leq 0.225$) in a high pressure device of “Toroid” type at hydrostatic pressures up to $P \leq 6$ GPa 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_xGeP₂ with ($x=0.09 \leq x \leq 0.225$) 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_xGeP₂ with ($x=0.09 \leq x \leq 0.225$) except the base CdGeP₂ 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_xGeP₂ with ($x=0.09 \leq x \leq 0.225$) of chalcopyrite structure near the T_c .

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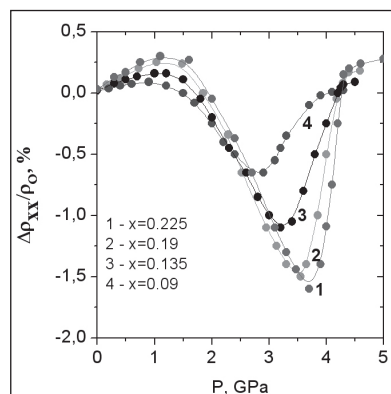


Fig.1. The baric dependence of transverse magnetoresistance ρ_{xx}/ρ_0 in a magnetic field $H=5$ kOe for Cd_{1-x}Mn_xGeP₂ with different level of Mn.

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Keywords: pressure, magnetic

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Crystal structure refinement of Pt-base perovskite

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$AA'_3B_4O_{12}$ -type perovskites have been extensively investigated because of their intriguing structural and physical properties. In $\text{CaCu}_3B_4\text{O}_{12}$ ($B = \text{Mn}^{4+}$ and Fe^{4+}) perovskites, electron carrier doping by substitution of an aliovalent cation La^{3+} for Ca^{2+} at A -site induces drastic changes in structural and physical properties [1], [2], [3], [4]. However, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ does not accept effective electron carriers by this type of substitution because of high stability of Ti^{4+} valence state in oxide. The resulting compound contains 1/3 deficiency at A -site, having a chemical formula of $\text{La}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ [5].

A novel Pt-based perovskite $\text{CaCu}_3\text{Pt}_4\text{O}_{12}$ (CCPO) has been reported [6]. CCPO is an antiferromagnetic insulator with $T_N = 40$ K. In the course of electron carrier doping for CCPO, we successfully obtained a $AA'_3B_4O_{12}$ -type perovskite phase from a nominal starting composition of $\text{LaCu}_3\text{Pt}_4\text{O}_{12}$ (LCPO). LCPO exhibited a spin-glass-like behavior below 4 K, whereas it remains an electrical insulator, suggesting that effective electron carriers were not introduced. Our structural refinement based on the synchrotron X-ray powder diffraction data implies that the LCPO has 1/16 deficiency at B -site, with the chemical formula of $\text{LaCu}_3\text{Pt}_{3.75}\text{O}_{12}$. LCPO is the first example that contains a significant amount of B -site cation deficiency in $AA'_3B_4O_{12}$ -type perovskite, suggesting that the possibility of B -site cation deficiency should be considered in the structural analysis of $AA'_3B_4O_{12}$ -type perovskite in some cases.

[1] Z. Zeng et al., *Phys. Rev. Lett.* **1999**, 82, 3164-3167. [2] J.A. Alonso et al., *Appl. Phys. Lett.* **2003**, 83, 2623-2625. [3] I. Yamada et al., *Angew. Chem. Int. Ed.* **2008**, 47, 7032-7035. [4] Y.W. Long et al., *Nature* **2009**, 458, 60-63. [5] A. Deshanvres et al., *Bull. Soc. Chim. Fr.* **1967**, 11, 4077-4078. [6] I. Yamada et al., *Inorg. Chem.* **2010**, 49, 6778-6780.

Keywords: platinum perovskite, vacancy, high-pressure synthesis

MS19.P11

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High pressure synthesis, structure, and physical properties of a novel iron-based perovskite $\text{YCu}_3\text{Fe}_4\text{O}_{12}$

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Iron-based perovskites $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Ca}^{2+}$ and La^{3+}), which were recently synthesized under high pressures of 10–15 GPa, demonstrate intriguing electronic phase transitions. $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ shows ferromagnetic and charge disproportionation (CD) transitions ($2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$) at 210 K [1]. In contrast, $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ (LCFO) exhibits

antiferromagnetic and intersite charge transfer (CT) transitions at 400 K, accompanied by a large volume change [2]. The essential factor determining the type of electronic phase transitions (CD or CT) has still been unsolved issue. To elucidate the above issue, we synthesized a novel perovskite $\text{YCu}_3\text{Fe}_4\text{O}_{12}$ (YCFO), in which large La^{3+} ion was substituted by small Y^{3+} ion, and studied the ionic size effect in the $A^{3+}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ perovskite.

YCFO was successfully synthesized at high pressure of 15 GPa. The synchrotron X-ray powder diffraction data in the temperature range of 100–450 K showed no abrupt volume change attributed to the CT, unlike LCFO. Magnetic susceptibility and isothermal magnetization data indicated a ferromagnetic transition at 250 K. ^{57}Fe Mössbauer spectra exhibited that a single $\text{Fe}^{3.75+}$ species of B -site at room temperature split into multiple magnetic sextets at 4 K, indicating the CD of $\text{Fe}^{3.75+}$ into Fe^{3+} and Fe^{5+} species ($8\text{Fe}^{3.75+} \rightarrow 5\text{Fe}^{3+} + 3\text{Fe}^{5+}$).

The above-mentioned electronic properties of YCFO, which are in contrast to those of LCFO, imply that the ionic size of A -site cation influences the electronic phase transition in $A^{3+}\text{Cu}_3\text{Fe}_4\text{O}_{12}$. We will discuss the ionic size effect, comparing the local structure of YCFO and LCFO.

[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, unusual high valence iron, high-pressure synthesis

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Novel high-pressure van der Waals compound in solid hydrogen-krypton mixtures

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Bonding interactions in molecular systems can be dramatically changed upon compression; atomic rare gases, diatomic (N_2 , O_2 , H_2 , etc.) and even full-shell molecules (CH_4 , SiH_4 , etc.) can interact with each other in solid form under high pressure; novel stoichiometric van der Waals compounds have been synthesised for example in the systems He-Ne [1], Ar- H_2 [2], CH_4 - H_2 [3], and more recently Xe- H_2 [4], [5].

The study of binary mixtures of hydrogen is of particular interest because they are relevant to the study of the interior of the giant planets and are of technological relevance for hydrogen storage.

Here we present a study of the binary system krypton-hydrogen. A diamond-anvil cell was loaded with a mixture of 8% in volume high purity Kr and H_2 . Kr and H_2 are miscible in the liquid phase. A solid phase with stoichiometry $\text{Kr}(\text{H}_2)_4$ was observed to form at a pressure of 5.3 GPa.

The structure of this novel van der Waals compound has been determined by single crystal diffraction at beamline I15, Diamond Light Source. Krypton atoms assemble in a face-centred cubic structure forming octahedral clusters with Kr-Kr bond distances comparable to the Kr bond distance in pure Kr solid.

Complementary Raman spectroscopic measurements were performed to better characterize the environment of the H_2 molecule. Three intramolecular H-H vibrons are observed at higher frequencies than those of pure, solid H_2 at the same pressure.

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