ISSN 0020-1685, Inorganic Materials, 2006, Vol. 42, No. 8, pp. 826–829. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.M. Novotortsev, A.Yu. Mollaev, I.K. Kamilov, R.K. Arslanov, U.Z. Zalibekov, S.F. Marenkin, S.A. Varnavskii, 2006, published in Neorganicheskie Materialy, 2006, Vol. 42, No. 8, pp. 916–918.

Phase Transformations of the Ferromagnetic Semiconductor $Cd_{1-x}Mn_xGeP_2$ at Pressures of up to 5 GPa

V. M. Novotortsev[a], A. Yu. Mollaev[b], I. K. Kamilov[b], R. K. Arslanov[b], U. Z. Zalibekov[b], S. F. Marenkin[a], and S. A. Varnavskii[a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia*

[b] *Institute of Physics, Dagestan Scientific Center, Russian Academy of Sciences, ul. Yaragskogo 94, Makhachkala, 367003 Dagestan, Russia*

e-mail: csq@mail.ru

Received October 21, 2005; in final form, February 28, 2006

Abstract—The electrical resistivity and Hall coefficient of $Cd_{1-x}Mn_xGeP_2$ (x = 0–0.19) have been measured at 300 K and hydrostatic pressures of up to 5 GPa. The results indicate that $CdGeP_2$ dissociates to CdP_2 and Ge at p = 3.2 GPa, while the incorporation of manganese stabilizes the crystal structure of $CdGeP_2$, and $Cd_{0.81}Mn_{0.19}GeP_2$ undergoes a reversible phase transition at p = 3.5 GPa.

DOI: 10.1134/S0020168506080036

INTRODUCTION

$Cd_{1-x}Mn_xGeP_2$ solid solutions are ferromagnetic semiconductors with Curie temperatures T_C above 300 K and are potentially attractive as spintronic materials [1, 2]. According to Demin et al. [2], their T_C increases with manganese content and reaches a maximum at the solubility limit of Mn in $CdGeP_2$. One way of increasing the solubility of an impurity is by raising the pressure. In connection with this, the purpose of this work was to determine pressures that induce irreversible phase transformations of $CdGeP_2$.

EXPERIMENTAL

We studied $Cd_{1-x}Mn_xGeP_2$ solid solutions with x = 0–0.19. Samples for this investigation were synthesized by reacting CdP_2 and Ge powders prepared from single crystals. Cadmium diphosphide crystals were grown as described by Trukhan et al. [3]. The impurity content of the high-purity single-crystal germanium used was within 0.1 ppm by weight. The Mn-containing samples were prepared using extrapure-grade manganese purified by double sublimation and V5 phosphorus. The starting-mixture compositions corresponded to the hypothetical join $CdGeP_2$–$MnGeP_2$. The starting mixtures (45–50 g) were placed in silica ampules coated with pyrolytic carbon, which were then pumped down to 10^{-2} Pa and sealed off.

Syntheses were performed in electrical furnaces equipped with heating blocks which ensured a uniform temperature profile along the entire length of the ampule: the temperature difference along the ampule was within 1°C. The samples were first heated to 450°C and held there for at least 48 h. Next, the temperature was gradually raised to 800°C at a rate no faster than 5°C/h and then maintained constant for at least 24 h. The cooling rate was 5 to 10°C/s. The Mn content of the samples was determined by atomic absorption. The analytical data agreed well with the nominal compositions.

The x-ray diffraction (XRD) patterns (DRON-1 diffractometer, Ni-filtered CuK_α radiation, 2θ = 10°–90°) of all the samples were similar to those of $CdGeP_2$, without peaks attributable to manganese phosphides. Comparison of peak positions in the XRD patterns of our samples with PDF data revealed a shift of the peaks to higher 2θ angles with increasing manganese content, indicating a reduction in lattice parameters. Increasing the Mn content from x = 0 to 0.09 and to 0.19 reduces the a parameter from 5.741 to 5.738 and to 5.667 Å, in agreement with the data reported by Medvedkin et al. [1].

Electrical resistivity and Hall effect measurements were carried out at hydrostatic pressures of up to 5 GPa in a Toroid anvil cell mounted in a multiturn solenoid which generated magnetic fields $H \leq 300$ kA/m. The sample surfaces were ground and etched. The sample dimensions were $3 \times 0.8 \times 0.8$ mm. Point contacts were

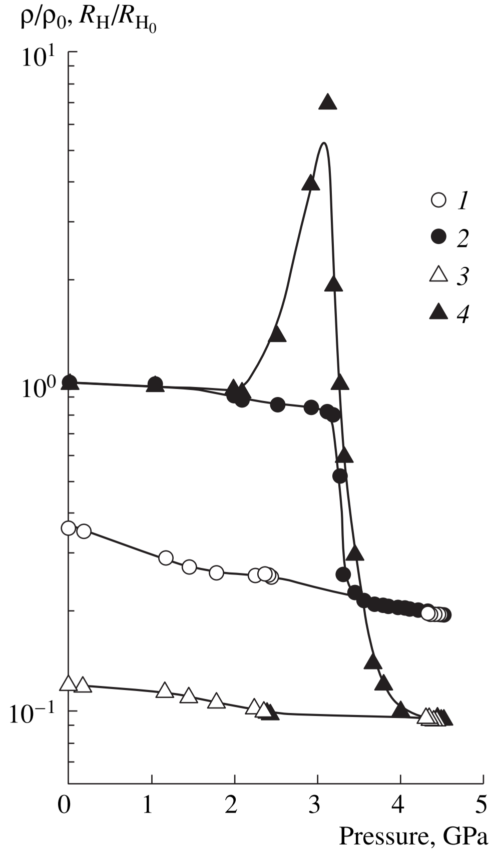

Fig. 1. (*1*, *2*) Resistivity and (*3*, *4*) Hall coefficient of $CdGeP_2$ as functions of (*2*, *4*) increasing and (*1*, *3*) decreasing pressure.

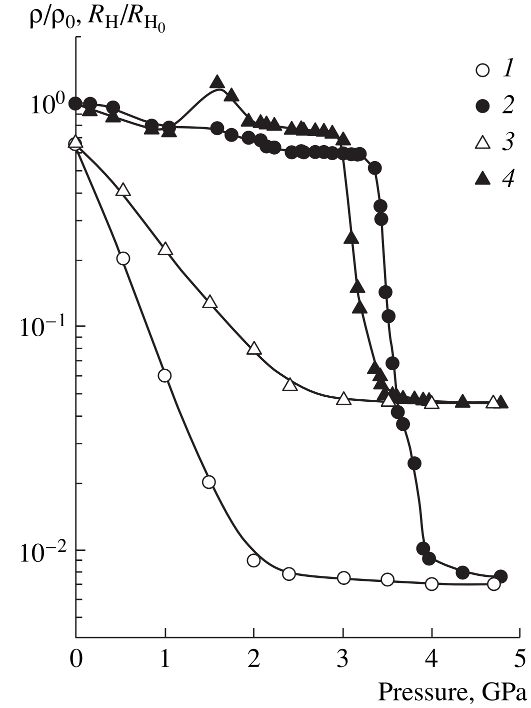

Fig. 2. (*1*, *2*) Resistivity and (*3*, *4*) Hall coefficient of $Cd_{0.91}Mn_{0.09}GeP_2$ as functions of (*2*, *4*) increasing and (*1*, *3*) decreasing pressure.

made by Sn. The uncertainties in resistivity ρ, Hall coefficient R_H, and pressure p were within ±3, 3.5, and 3%, respectively.

RESULTS AND DISCUSSION

The electrical properties of our samples are summarized in the table. All of the samples were *p*-type. With increasing Mn content, the carrier concentration in the samples and their electrical conductivity increase, with no type conversion.

Figure 1 shows the resistivity (curves *1*, *2*) and Hall coefficient (curves *3*, *4*) of $CdGeP_2$ as functions of increasing (curves *2*, *4*) and decreasing (curves *1*, *3*) pressure. The resistivity of $CdGeP_2$ decreases only gradually with increasing pressure below 3.2 GPa and then drops sharply, by almost one order of magnitude. Starting at $p = 4$ GPa, ρ varies little with pressure. The behavior of R_H is similar to that of resistivity. The $\rho(p)$ and $R_H(p)$ data obtained during loading and unloading differ markedly. During unloading, the ρ and R_H of $CdGeP_2$ are linear functions of p. By analogy with earlier results [4], we conclude that $CdGeP_2$ dissociates at 3.2 GPa, as supported by XRD data: after unloading, the XRD pattern of the sample shows peaks from CdP_2 and Ge.

Figure 2 shows the resistivity and Hall coefficient of $Cd_{0.91}Mn_{0.09}GeP_2$ as functions of increasing and decreasing pressure. The resistivity gradually decreases with increasing pressure below ~3.3 GPa and then drops sharply, by almost two orders of magnitude. At $p > 3.5$ GPa, ρ varies little. The behavior of R_H is similar to that of resistivity. The reverse (unloading) $\rho(p)$ and $R_H(p)$ curves of $Cd_{0.91}Mn_{0.09}GeP_2$ differ in shape from those of $CdGeP_2$. During unloading, the phase transformation of the $Cd_{0.91}Mn_{0.09}GeP_2$ sample occurs at $p = 2.3$ GPa. Since the $\rho(p)$ and $R_H(p)$ measured

Transport properties of $Cd_{1-x}Mn_xGeP_2$ samples (*p*-type conductivity)

Composition	R_H, cm^3/C	N, cm^{-3}	ρ, Ω cm	μ, $cm^2/(V\ s)$
$CdGeP_2$	73.1	8.5×10^{16}	27.5	2.6
$Cd_{0.91}Mn_{0.09}GeP_2$	20	3.12×10^{17}	3.02	6.6
$Cd_{0.81}Mn_{0.19}GeP_2$	3	2.08×10^{18}	0.72	4.2

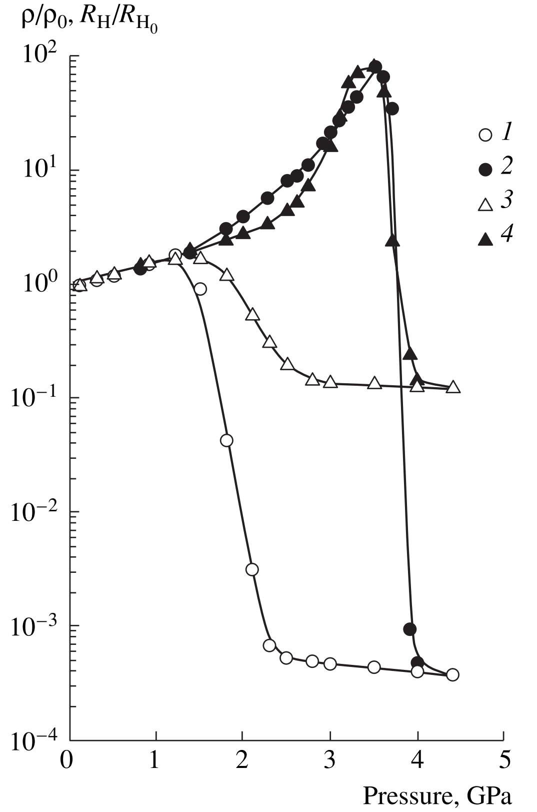

Fig. 3. (*1*, *2*) Resistivity and (*3*, *4*) Hall coefficient of $Cd_{0.81}Mn_{0.19}GeP_2$ as functions of (*2*, *4*) increasing and (*1*, *3*) decreasing pressure.

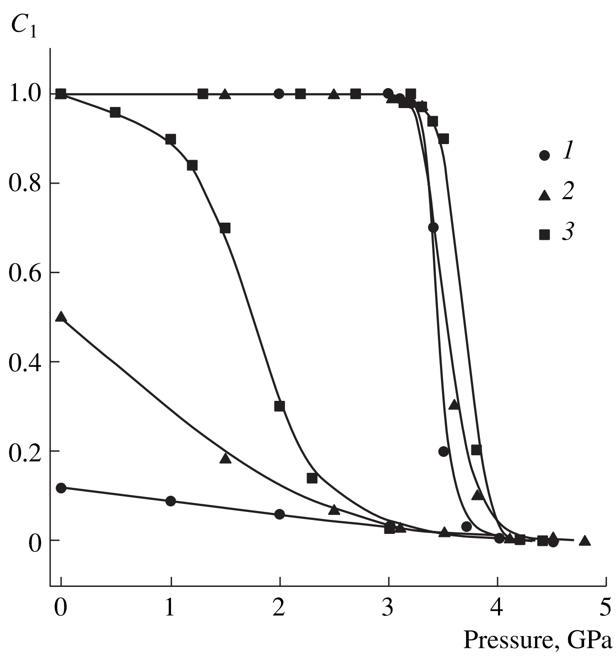

Fig. 4. Volume fraction of the parent phase as a function of increasing and decreasing pressure for (*1*) $CdGeP_2$, (*2*) $Cd_{0.91}Mn_{0.09}GeP_2$, and (*3*) $Cd_{0.81}Mn_{0.19}GeP_2$.

before and after the loading–unloading cycle differ slightly, the phase transition seems to be accompanied by partial dissociation of the sample.

Figure 3 shows the resistivity and Hall coefficient of $Cd_{0.81}Mn_{0.19}GeP_2$ as functions of increasing and decreasing pressure. Both the resistivity and Hall coefficient slightly increase with pressure before reaching a maximum at p = 3.5 GPa and then drop sharply, by almost six and two orders of magnitude, respectively. Note that the ρ and R_H measured before and after the loading–unloading cycle coincide. During unloading, the phase transition occurs at p = 2.3 GPa. Thus, this sample undergoes a reversible structural phase transition at p = 3.5 GPa, as supported by XRD data: after unloading, the XRD pattern of $Cd_{0.81}Mn_{0.19}GeP_2$ showed only peaks from $CdGeP_2$.

Comparison of the resistivity and Hall coefficient versus pressure data for $CdGeP_2$ (Fig. 1), $Cd_{0.91}Mn_{0.09}GeP_2$ (Fig. 2), and $Cd_{0.81}Mn_{0.19}GeP_2$ (Fig. 3) indicates that the incorporation of Mn extends the pressure stability range of the material: $CdGeP_2$ dissociates at 3.2 GPa, $Cd_{0.91}Mn_{0.09}GeP_2$ partially dissociates at 3.3 GPa, and $Cd_{0.81}Mn_{0.19}GeP_2$ undergoes a reversible structural phase transition at 3.5 GPa. This is supported by XRD data: as the Mn content increases, the XRD patterns of the samples show, in addition to peaks from CdP_2 and Ge, those from $CdGeP_2$.

To analyze the variation in the volume fraction of the parent phase, C_1, we considered a mixed-phase system–effective medium model [5]. It can be seen in Fig. 4 that, after one loading–unloading cycle, C_1 is 0.1 in $CdGeP_2$, 0.5 in $Cd_{0.91}Mn_{0.09}GeP_2$, and 1 (fully reversible process) in $Cd_{0.81}Mn_{0.19}GeP_2$.

CONCLUSIONS

The present $\rho(p)$, $R_H(p)$, and XRD data indicate that $CdGeP_2$ dissociates to CdP_2 and Ge at p = 3.2 GPa. The incorporation of Mn stabilizes the crystal structure of $CdGeP_2$, and $Cd_{0.81}Mn_{0.19}GeP_2$ undergoes a reversible phase transition at p = 3.5 GPa.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 05-03-33068 and 05-02-16608) and the Presidium of the Russian Academy of Sciences (project *Physics and Mechanics of Heavily Compressed Matter and the Internal Structure of the Earth and Other Planets*).

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