Physics of the Solid State, 2025, Vol. 67, No. 11

03,11

High-pressures relaxation effects in *n*-CdAs$_2$

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Received September 25, 2025
Revised September 27, 2025
Accepted November 15, 2025

Experimental studies of the baric dependences of the electrical and magnetoresistance of n-CdAs$_2$ at pressures up to 50 GPa and in magnetic fields up to 1 T are reported. High values of negative magnetoresistance (up to 8 %) is shown to form with pressure. Relaxation effects caused by plastic deformation of materials are investigated. Within 25−35 GPa, a significant increase in the relaxation time of electrical resistance is observed, apparently due to an extended metastable states and structural transition type-I. The structural transformation is also reflected in the electronic subsystem, which leads to minima increasing with the magnetic field on the baric dependences of the magnetoresistance.

Keywords: high pressure, relaxation effects, electrical resistance, magnetic resistance, magnetic field, phase transitions.

DOI: 10.61011/PSS.2025.11.62952.118-25

1. Introduction

Study of electrical resistance of semiconductor compounds under high pressures makes it possible to obtain information on the potential structural polymorphous transformations, which is of both fundamental and applied interest, in particular, in calibration of high pressure chambers. It should be taken into account that the phase transition in semiconductors happens in a certain pressure range. This is due to a combination of various inhomogeneities, besides, the properties of semiconductors vary even when the pressure is stable, i. e. there is time dependence observed, for example, of electrical resistance on time at a certain constantly applied pressure. Therefore a certain time is required for the crystalline structure to change from a non-equilibrium to an equilibrium state. Under heterogeneous deformation, arising from non-hydrostaticity or quasi-hydrostaticity of the applied pressure, the number of point defects, dislocations, admixtures increases substantially, especially in the baric area of structural transitions, therefore quite a long time is required, so that the concentration of defects decreased due to annihilation of an interstitial atom with a vacancy, annihilation of vacancies, removal of elastic stresses etc. processes of structual relaxation.

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The pressure changes the distance between atoms and their environment that can originates new carriers etc. Using the dependences of electrical resistance on the time of application of the constant load, one can study in detail the relaxation processes that arise from pressure treatment. Relaxation times increase sharply near the phase transitions, reaching from dozens of seconds to dozens of minutes.

Sharp increase of the relaxation time of physical parameters indicates structural and phase transformations [1–3]. At the same time usually the dynamics of electrical resistance variation after pressure application is described by exponential dependence, which makes it possible to easily calculate the electrical resistance relaxation time.

It is known that at critical pressure, i. e. pressure close to the pressure that induces a phase transition, critical moderation of structural relaxation is observed, therefore, the relaxation time increases sharply, and directly in process of phase transitions the kinetics of electrical resistance stops being described by an exponent [4–6].

It turned out that the best object to study relaxation phenomena in a semiconductor, both in the area of structural phase transitions and beyond, i. e. in the area of a metastable structural and highly defective state, was a single-crystal n-CdAs$_2$. CdAs$_2$ — a semiconductor with a moderate width of the band gap — differs by high anisotropy of optical (the double refraction in the infrared area is especially interesting), electric and thermoelectric properties. Recently it has been reported as a promising candidate for demonstration of new topological properties protected by the structural chirality of the system and as the basic material for the innovative spintronic and optical devices using quantized chiral charges and negative longitudinal magnetoresistance [7,8]. It is important that both poly- and mono-crystal phases were studied well, which makes it possible to certainly match the detected relaxation effects to the structural transitions and corresponding metastable and defective states [9–11]. The Cd–As system state diagram was studied thoroughly [12–15]. The study of this system was stated by S.F. Zhemchuzhny [12], who demonstrated that the system included two stable congruent melting compounds Cd_3As_2 and $CdAs_2$. The true equilibrium diagram of the system state determined as a result of the thorough study with account of the differences between all prior studies presented by H. Okamoto in 1992 [13] found two stable congruent melting compounds: Cd_3As_2 with melting point of 994) and $CdAs_2$ with melting point of 894 K. However, crystallization of the latter may be suppressed, which causes metastable states [13]. Due to the above, this paper is dedicated to the study of baric dependences of electrical resistance and relaxation phenomena n-$CdAs_2$ under the conditions of exposure to high pressures (up to 50 GPa) and magnetic fields (up to 1 T).

2. Samples and experimental procedure

Single crystals of cadmium diarsenide were produxed by the method of directional solidification of the melt using the Bridgman's method [16]. The impact of high pressure at electrophysical properties of composites was studied in the high pressure chamber (HPC) with diamond anvils of „rounded cone–plane" type. Schematic image of the HPC in section in Figure 1.

The principle of building pressures up to 50 GPa, technical characteristics and calibration of HPC are described in detail in [17–19]. The used equipment makes it possible to measure electrical characteristics of the material directly in the process of deformations when high pressures are applied. In connection with the HPC features, the minimum pressure, when electrophysical characteristics of compressed samples may be measured, may not be below 15 GPa. Besides, it is known that when pressure changes (increases or decreases), a certain time is required for the electrical resistance to be established as constant in time. The thickness of samples under compression was $\sim 15\,\mu$m, the sample diameter in HPC was around $\sim 200\,\mu$m.

To assess the role of relaxation effects caused by plastic deformation of materials, at certain fixed values of the applied load (at pressure increase and subsequent decrease) the dependences of electrical resistance R on time of exposure to the load τ were measured, analyzing the behavior of dependences $R(\tau)$. Besides, the value of the relative change of electrical resistance was also estimated at every pressure value from the studied range (with the new load applied), in the following manner.

$$\frac{\Delta R}{R} = \frac{R(\tau_{\mathrm{rel}}) - R(\tau_0)}{R(\tau_0)}, \tag{1}$$

where $\tau_0 = 0$ — the moment of time of actual application of the new load at the sample, τ_{rel} — time when the constant value of electrical resistance is set after application of a new fixed load.

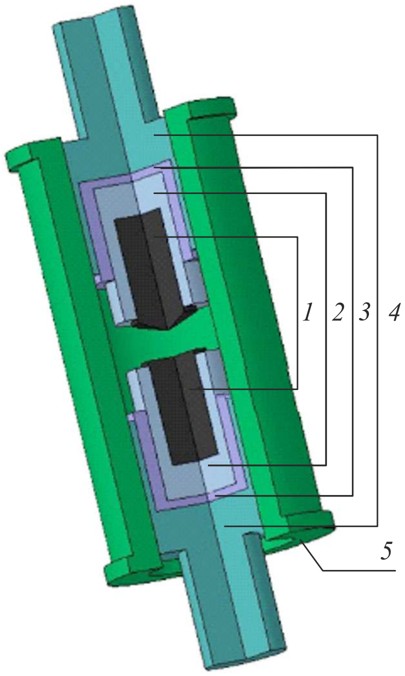

Figure 1. Schematic image of high pressure chamber in section: *1* — anvils, *2* — shells, *3* — insulator, *4* — inserts, *5* — cylinder.

To measure magnetoresistance, the high pressure chamber was placed into an armor-clad electromagnet, which created transverse magnetic field from 0 and to 1 Tl at each fixed pressure value the relative magnetoresistance MR in % was estimated using formula

$$MR = 100\,\% \cdot \frac{R(B) - R(0)}{R(0)}, \tag{2}$$

where $R(B)$ — electrical resistance in the transverse magnetic field with induction B, $R(0)$ — electrical resistance in the absence of the magnetic field.

3. Results and discussion

Figure 2 shows the results of measurement of the baric dependence of electrical resistance $R(P)$ n-$CdAs_2$ at room temperature up to 50 GPa. Several cycles of pressure compression-decompression were carried out. The chart shows two complete cycles of increase and decrease of the pressure applied to the same sample. Pressure cycling and tracking of reversibility of the observed changes demonstrated that there was always a certain hysteresis between the values of electrical resistance as the pressure increased and decreased. Hysteresis was due to the change in the sample volume in compression and decompression processes. The second and subsequent cycles have the minimum width of the hysteresis loop and do not change as the number of cycles increases.

From the chart $R(P)$ you can see that for the first pressure increase you may identify three areas, where monotonic dependences close to a linear one are observed: 16–28, 30–38 and 42–50 GPa.

A curve corresponding to pressure reduction is also broken into three linear sections, but with other boundaries this time: 16–22, 22–38 and 38–50 GPa. Such pressure hysteresis is observed in many compounds and is probably related to the existence of metastable states in decompression. A repetitive loading branch qualitatively repeats the first loading chart, except for a minor shift of pressures corresponding to the boundaries of linear sections. In the pressure range from 16 to 50 GPa n-CdAs$_2$ experiences two structural changes that are fully reversible and reproducible in subsequent barocycling.

Dependences of electrical resistance on time $R(\tau)$ at fixed pressure are approximated well by one (at $\tau_1 = \tau_2$) or two exponents:

$$R(\tau) = A_1 e^{-\tau/\tau_1} + A_2 e^{-\tau/\tau_2}, \tag{2}$$

where τ — time after external pressure change, τ_1 and τ_2 — conductivity relaxation times [5]. Shorter time $\tau_{\text{min}} = Min\{\tau_1, \tau_2\}$ corresponds to relaxation processes related to the change in the concentration of carriers and band gap width as a result of distances change between atoms and change of carriers energy. Longer time $\tau_{\text{max}} = Max\{\tau_1, \tau_2\}$ characterizes the processes caused by relaxation of structural defects in the crystalline lattice. Besides, even though the most adequate is approximation (2), approximation with a single exponent is also performed:

$$(\tau) = Ae^{-\tau/\tau_{\text{med}}}. \tag{3}$$

In equation (3) τ_{med} — so called „average“ relaxation time, in a general case matching τ_1 and τ_2 in equation (2) at $\tau_1 = \tau_2$ and different both from τ_1 and from τ_2 at $\tau_1 \neq \tau_2$. The completed estimation of the average relaxation time τ_{med} using Eq. (3) enables determining preferable processes in the material: if it is close to τ_{min}, processes prevail that are related to the change in parameters of carriers, if τ_{med} is close to τ_{max}, processes prevail that are related to the relaxation of the crystalline lattice structure (under exposure to high pressure). The obtained dependence $R(\tau)$ for n-CdAs$_2$ at pressure of 44 GPa is presented in Figure 3.

This dependence $R(\tau)$ is described by Eq. (2). Similarly time dependences of electrical resistance were approximated for all pressures. Dependence τ_1 of the first relaxation time of electrical resistance on pressure $\tau_1(P)$ is presented in Figure 4. Dependences are shown for two pressure increase cycles. The highest relaxation times τ_{max} of electrical resistance are recorded in the pressure area of 22–30 GPa specific for structural transformation in cadmium diarsenide (Figure 4).

During the first cycle of pressure increase it is possible to identify two peaks of relaxation time τ_1. The first peak corresponds to pressure of 30 GPa, the relaxation time then increases approximately by an order of magnitude compared to times up to 28 GPa and reaches 1800 s. The peak is

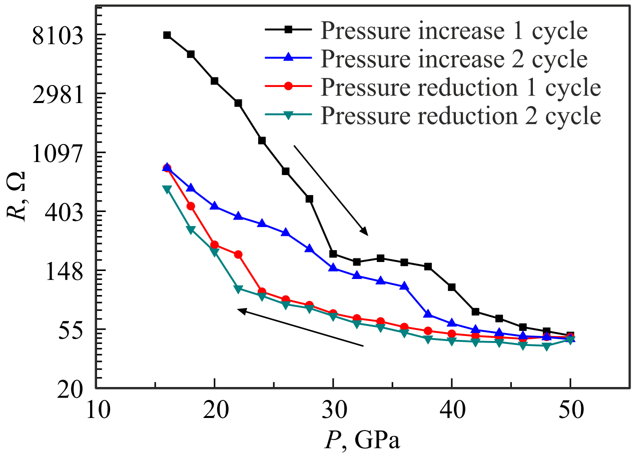

Figure 2. Electrical resistance n-CdAs$_2$ depending on pressure.

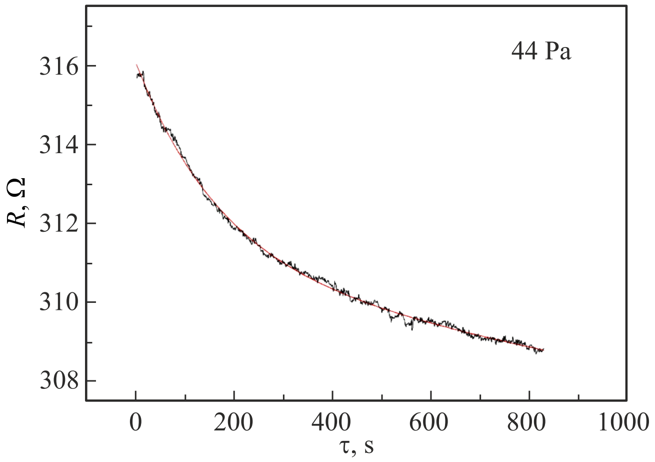

Figure 3. Dependence $R(\tau)$ at pressure 44 GPa for n-CdAs$_2$.

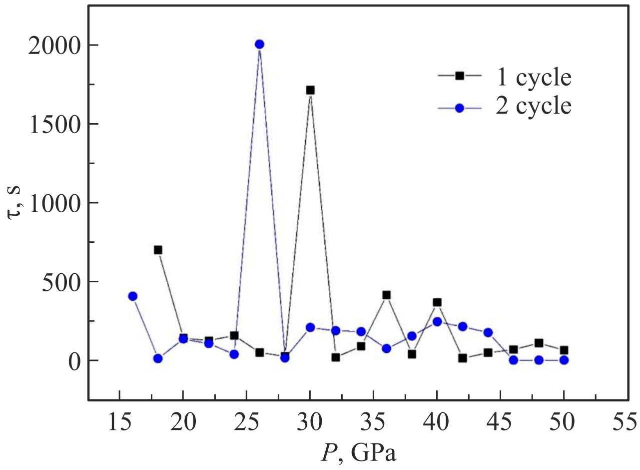

Figure 4. Dependence of electrical resistance relaxation time on pressure $\tau(P)$ for two loading cycles of sample n-CdAs$_2$.

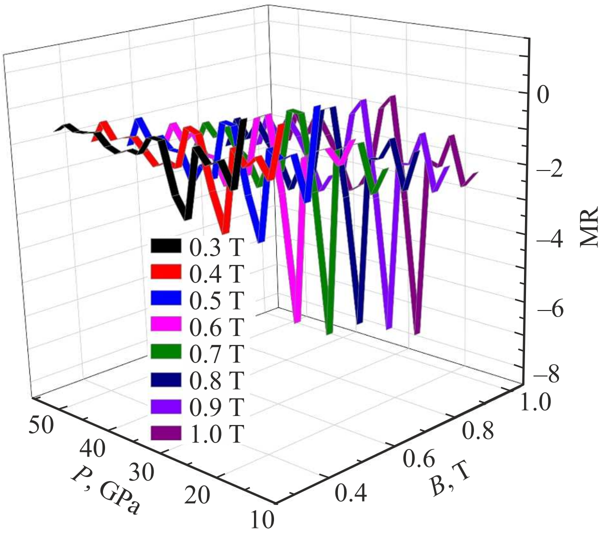

Figure 5. Baric dependences of magnetoresistance n-CdAs$_2$.

quite narrow, already at 32 GPa there is a drastic drop in relaxation time to the initial values. The second peak arises at pressures of 36−40 GPa. It is not so intense and narrow as the first one, the relaxation time increases only 2−3 times compared to the initial one. In the second cycle of pressure increase the first peak is maintained and shifted to the area of low pressures down to the values of 26 GPa. And the area corresponding to the second peak is not so pronounced as during the first loading. The second peak pressure range may be specified from 36 to 46 GPa.

For the second relaxation time of electrical resistance τ_2, corresponding to slower processes, the total dependence is maintained the same as for τ_1. At pressures of 30−32 and 40−42 GPa approximation provides no satisfactory results for determination of value τ_2.

As pressure rises, CdAs$_2$ is characterized by manifestation of negative values of magnetoresistance (MR). In the pressure interval of $P = 24-27$ GPa and at $P = 34-40$ GPa there are two local extrema in curves $MR(P)$. In the baric interval of (24−27) GPa and at (34−40) GPa, CdAs$_2$ demonstrates high values of MR, accordingly to 8 % and 4 % in the field 1 T. With further pressure increase, after the area of global extremum in curve $MR(P)$, magnetoresistance remains negative up until 50 GPa.

Decrease of electrical resistance with increase of the magnetic field induction was observed in the study of electrical properties of CdAs$_2$ at pressures of up to 9 GPa [20] and approximately at 5.5 GPa in CdAs$_2$ they observed phase transition manifestations.

4. Conclusions

The study of relaxation effects at barocycling of electrical resistance n-CdAs$_2$ in the pressure interval of up to 50 GPa found a drop in electrical resistance value in the second cycle of application−removal of pressure by more than an order of magnitude, with stronger manifestation of abnormalities assigned to two structural phase transitions at 20 and 36 GPa, and an area of metastability between these transitions.

The study of relaxation effects at barocycling the electrical resistance of n-CdAs$_2$ in the pressure interval of up to 50 GPa found a drop in electrical resistance value in the second cycle of application-removal of pressure by more than an order of magnitude, with stronger manifestation of abnormalities assigned to two structural phase transitions at 20 and 36 GPa, and an area of metastability between these transitions.

Analysis of baric dependences of n-CdAs$_2$ electrical resistance relaxation times made it possible to identify two areas of pressures corresponding to two structural phase transitions in areas of 16−28 and 34−38 GPa, respectively, and the area between these phase transitions, corresponding to a metastable state of two structural modifications. In the area of structural phase transitions the electrical resistance relaxation time increases by more than an order of magnitude, which agrees with the theory of structural phase transitions and, thus, additionally to our prior research, confirms that in n-CdAs$_2$ two structural transitions happen in areas of 16−28 and 34−38 GPa. These structural transitions recur in repetitive barocycling and are therefore reproducible and reversible and, accordingly, are not related to quality, i. e. with sample compaction at high pressures.

In the pressure area of 16−28 GPa negative magnetoresistance is found to rise from 2 % at 0.4 T to a record one for n-CdAs$_2$ — 8 % at 1 T.

Funding

The study was partially supported by the state assignment of the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

Conflict of interest

The authors declare no conflict of interests.

References

[1] M.R. Collins. Phys. Rev. Lett. American Physical Society **30**, *17*, 781 (1973).
[2] S. Kazlauskas. Electrochim. Acta. **134**, 176 (2014).
[3] I. Hatta. J. Phys. Soc. Japan. **28**, *5*, 1266 (1970).
[4] T. Hashimoto, K. Nishimura, Y. Takeuchi. J. Phys. Soc. Japan. **45**, *4*, 1127 (1978).
[5] T. Mohri, M. Ohno. Philos. Mag. **83**, *3*, 315 (2003).
[6] N. Wakabayashi. Phys. Rev. B **33**, *9*, 6441 (1986).
[7] F. Mazzola, Y. Zhang, N. Olszowska, M. Rosmus, G. D'Olimpio, M.C. Istrate, A. Politano. J. Phys. Chem. Lett. **14**, 3120 (2023).
[8] Y. Zhang, G. D'Olimpio, F. Bondino, S. Nappini, M.C. Istrate, R. Sankar, A. Politano. Appl. Sur. Sci. **625**, 157132 (2023).

[9] L.A. Saypulaeva, Sh.B. Abdulvagidov, A.V. Tebenkov, S.F. Marenkin. High Pressure Research, in print (2025).
[10] B. Shipilo, E.M. Plyshevskiy, I.M. Belsky. Physics of gas and solid-Phase pressures (Nauka, Moscow, 1978).
[11] J.B. Clark, C.W.F.T. Pistorius. High Temp. High Press. **5**, 319 (1973).
[12] S.F. Zemczuzny. Int. Z. Metallogr. **4**, 228 (1913).
[13] H. Okamoto. JPE **13**, 147 (1992).
[14] S.F. Marenkin, V.M. Trukhan. Fosfidy, arsenidy tsinka i kadmiya (Zinc and Cadmium Phosphides and Arsenides) (Nauchno-Prakticheskii Tsentr Natsional'noi Akad. Nauk Belarusi, Minsk, 2010). (in Russian).
[15] O. Kidari, P. Chartrand. Metall Mater Trans B **54**, 2793 (2023).
[16] S.F. Marenkin, A.M. Raukhman, A.B. Maymasov, V.A. Popov. Neorgan. Materialy **33**, *12*, 1439 (1997). (in Russian).
[17] D.L. Decker. J. Appl. Phys. **42**, *8*, 3239 (1971).
[18] A.N. Babushkin. Elektroprovodnost i termoEDS galogenidov schelochnykh metallov i drugikh materialov pri davleniyakh 20−50 GPa. Uralsky gosudarstvennyi universitet im. A.M. Gorkogo (1992). (in Russian).
[19] A. Onodera, N. Kawai, K. Ishizaki, I.L. Spain. Solid State Commun. **14**, *9*, 803 (1974).
[20] A.Y. Mollaev, L.A. Saypulaeva, R.K. Arslanov, S.F. Gabibov, S.F. Marenkin. High Pressure Research **22**, 181 (2002).

Translated by M.Verenikina