

THERMOELECTRICAL PROPERTIES OF Mn-DOPED n-Cd₃As₂I.K. KAMILOV¹, L.A. SAIPULAEVA¹ N.V. MELNIKOVA², A.I. RIL³,
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The paper reports the findings on the baric dependences of the thermoelectromotive force (thermo-emf) of the Cd₃As₂ + *n* mol% MnAs granular structures, *n*=10, 20, 30 and 44.7, where peculiarities in the thermo-emf behavior (extrema, inflection points on the S(P) curves or pressure hysteresis) are observed. The peaks are observed in Cd₃As₂ + *n* mol% MnAs in the pressure range P= (28-35) GPa for the cases *n*=10 and *n*=20; in Cd₃As₂ + 30 mol. % MnAs at P= (20-35) GPa; in Cd₃As₂ + 44.7 mol. % MnAs at P=(30-35) GPa. At pressures higher than 40 GPa, the thermo-emf changes weakly or practically does not vary both at increasing and subsequent decreasing pressures.

Keywords: thermoelectromotive force, electric resistance, clusters, high pressures, Seebeck coefficient, relaxation time.

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INTRODUCTION

The Dirac Cd₃As₂ semimetal has drawn the attention of researchers with its intriguing properties: nontrivial zone structure [1], unusually high electron mobility, much higher than 10⁴ cm²/(B·s) at room temperature and 10⁶ cm²/(B·s) at low temperatures [2]. Despite its high mobility, the Cd₃As₂ thermal conductivity is found to be lower than 4.17 W/m·K [3]. The temperature dependence of the electrical resistivity in typical monocrystal Cd₃As₂ reveals a behavior of a semimetal with saturation at low temperatures and metallic type of the conductivity. The study of Seebeck coefficient (S) in [3] shows the negative sign of S indicating electronic type of the conductivity. The S value achieves 74.1 μV/K at room temperature. The temperature dependence of the Seebeck coefficient S(T) is linear over a wide temperature range (2-380 K) [3]. The characteristics of electrical resistivity and thermo-emf of Cd₃As₂ thin films with 700 nm in thick investigated in [4] are slightly different from the corresponding characteristics for bulk samples. When temperature grows, the specific electrical resistivity first increases and then begins to fall at T = 30K. The temperature dependence of the thermo-emf (S) in [4] confirms the thermal activation process. At low temperatures, the positive sign of S specifies that holes

are the dominant carriers, while at T>57 K, the sign of S becomes negative indicating that thermally activated electrons become the dominant carriers.

Cd₃As₂ containing MnAs magnetic granules are attractive for spintronics, since these structures consist of alternating magnetic and nonmagnetic nanodomains and are distinguished by highly mobile electrons. The fundamental interest in the study of such structures is determined by a significant role of magnetic exchange interactions in them along with the known and widely studied interactions in semiconductor structures.

This work presents a study of the thermoelectric properties of Cd₃As₂ + *n* mol% MnAs, *n*=10, 20, 30, and 44.7, in particular, the behavior of the Seebeck coefficient versus pressure. Previously, the magnetization, the electrical resistivity, the Hall coefficient and their temperature dependences were researched in structures of similar composition [5-7].

The aim of the work is to evaluate the effect of pressure on the thermoelectric properties of Cd₃As₂ + *n* mol% MnAs, *n*=10, 20, 30, and 44.7.

TECHNIQUE OF THERMO-EMF RESEARCH

Bulk samples of Cd₃As₂ - MnAs were obtained at the N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences [8].

Table 1.

Composition of synthesized samples of Cd₃As₂ - MnAs system [8]

№ of sample	Content of MnAs, mole %	Elemental composition of samples according to EDRS results, at.%		
		Cd	As	Mn
1	10	58.7	39.9	1.4
2	20	51.3	41.4	7.3
3	30	50.3	41.5	8.2
4	44.7	48.6	40.0	11.4

The composition of some samples is given in Table 1 [8].

Pressures up to 50 GPa were created in high-pressure chambers (HPC) with anvils made of artificial diamonds of the “carbonado” type, which are good conductors and allow one to research the electrical properties of samples placed in HPC.

The mechanism of generating pressures up to 50 GPa, technical characteristics and calibration of HPCs were described in detail in [9-11].

The principle scheme of thermo-emf measurements in a high-pressure chamber with anvils of the “rounded cone-plane” type was detailed in [12]. All measurements were carried out at room

temperature. The temperature gradient across the sample did not exceed 1 K.

RESULTS AND DISCUSSIONS

Diffraction patterns of $Cd_3As_2 + n \text{ mol } \% \text{ MnAs}$ granular structures $n=10, 20, 30$ and 44.7 are depicted in Fig. 1. The main phases are Cd_3As_2 and MnAs, and also it can be mentioned the existence of $CdAs_2$ phase in residual amounts.

Electron microscopic analysis of $Cd_3As_2 + n \text{ mol } \% \text{ MnAs}$ allowed to detect the presence of MnAs particles from 5 to 110 nm in $Cd_3As_2 + 44.7 \text{ mol } \% \text{ MnAs}$ (Figure 2 d).

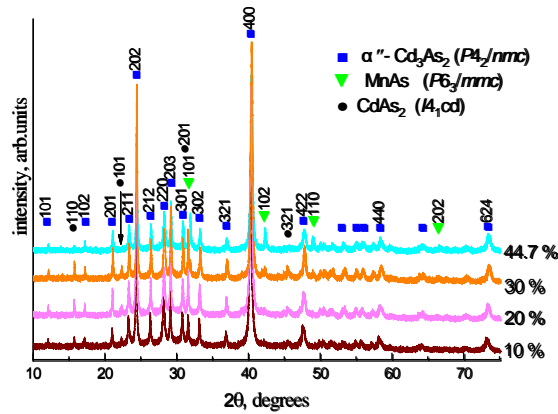


Fig. 1. X-ray patterns of $Cd_3As_2+n \text{ mol}\% \text{ MnAs}$ samples.

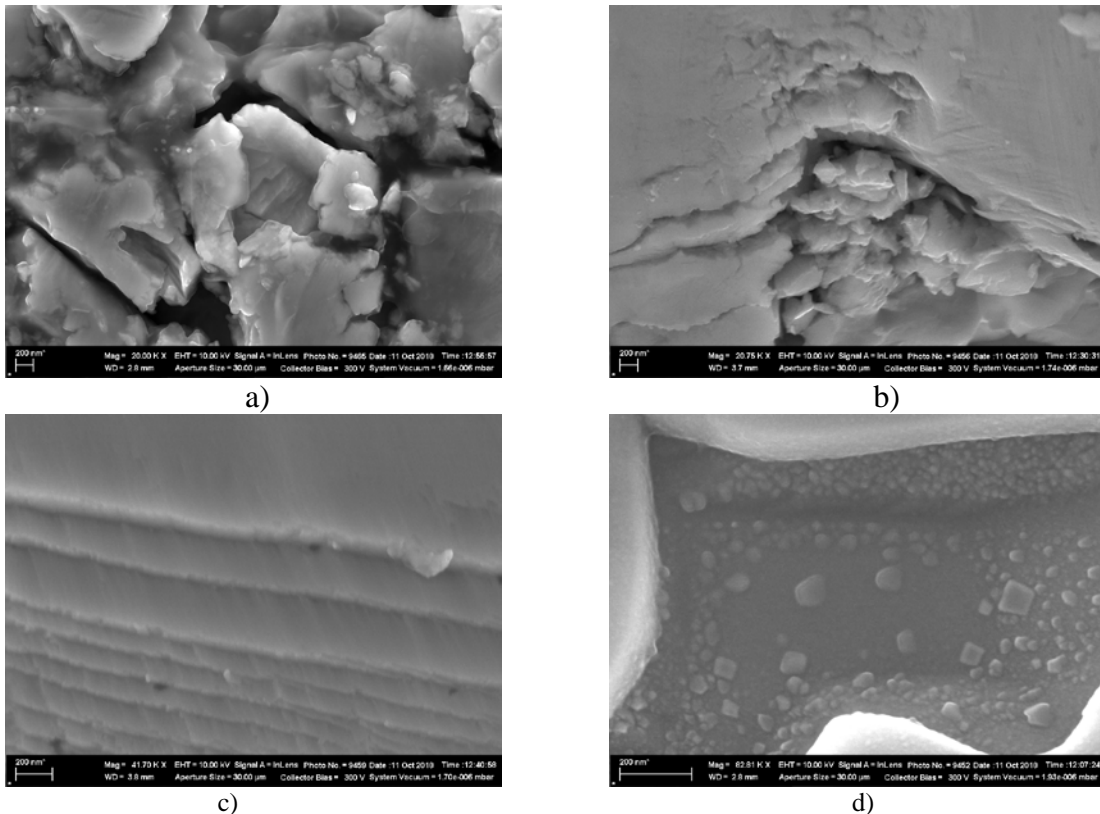


Fig. 2. SEM images of splittings of $Cd_3As_2 + n \text{ mol}\% \text{ MnAs}$ samples a) $n=10$, b) $n=20$, c) $n=30$, d) $n=44.7$

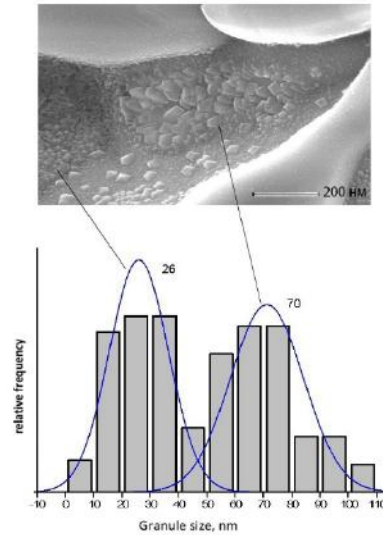


Fig. 3. Size distribution of MnAs nanoclusters in the $\text{Cd}_3\text{As}_2+44.7$ mol% MnAs composite and one example of the SEM images of a sample spall/chip.

At $n < 44.7$, the granules failed to be visualized in electron microscopic investigations (Figure 2 a, b, c), probably because of their small size. The analysis of MnAs nanocluster sizes in the granulated $\text{Cd}_3\text{As}_2 + 44.7$ mol % MnAs revealed a “two-humped” (bimodal) particle size distribution: characteristic diameters of MnAs nanoclusters are 20-30 nm and 50-90 nm (Figure 3).

It is most likely that particles larger than 50 nm can be located in the near-surface regions rather than in the material volume, as the opposite would lead to a significant increase in the deformation energies of both the matrix itself and the nanoclusters.

Proceeding from this, one can expect that the bulk physical properties of the granulated $\text{Cd}_3\text{As}_2+44.7$ mol % MnAs may be determined by the properties of MnAs nanoclusters with 20-30 nm in size. Previously, the nanocluster sizes of the order 30-50 nm was reported for $\text{Cd}_3\text{As}_2+80$ mol % MnAs, and their size was estimated with the Debye-Scherrer formula, using the obtained X-ray diffraction patterns and taking into account the small value of the coercivity (less than 20 E) estimated from the magnetic field dependences [13]. Applying the method of magnetic force microscopy, the authors [8] succeeded in determining the presence of magnetic inclusions for Cd_3As_2+n mol % MnAs samples with MnAs content above 10 mol%, and the concentration and size of magnetic impurity inclusions grew as the Mn content increased. For instance, the average size of MnAs granules in the $\text{Cd}_3\text{As}_2 + 70$ mol % MnAs material was 50 nm.

Thus, the materials $\text{Cd}_3\text{As}_2 + n$ mol % MnAs are granulated structures consisting of nanosize ferromagnetic MnAs granules (whose sizes decrease with decreasing n , which is coincided with the conclusions of work [8]) chaotically located in the volume of the Cd_3As_2 semiconductor matrix.

Investigations on the baric dependences of the Seebeck coefficient for $\text{Cd}_3\text{As}_2 + n$ mol% MnAs composites are carried out by the following scheme: we gradually increase the pressures from ~ 4 GPa to the maximum ~ 50 GPa at certain baric intervals, keeping

the sample for some time at each value of the increasing pressure before taking the measurement, and then at the subsequent gradual decrease in pressure to the initial one. Data on the transport properties of granulated structures at pressures up to 50 GPa clarified that the main carriers at high pressures up to 50 GPa are holes in Cd_3As_2+n mol%MnAs samples ($n = 10, 20, 30$) in the material with $n=44.7$ are electrons. The Seebeck coefficient value and its sign for the structure with $n=44.7$ are typical for the investigated material, which is a semiconductor matrix (Cd_3As_2 is an n-type narrow-gap semiconductor) with ferromagnetic MnAs granules. The measurement results are summarized in Figure 4. For materials with a lower content of MnAs granules, hole carriers are predominant under pressure exceeding 3 GPa. On the coexistence of hole and electron carriers and the asymmetry in their mobility (associated with the zone structure) were reported by the authors [14, 15] when exploring the properties of Cd_3As_2 thin (200-700 nm thick) monocrystal films and by the authors [1] when conducting theoretical studies of the zone structure of Cd_3As_2 crystals. The effect of the predominance of hole carriers on the surface and electron carriers in the material volume was discussed in [15] when studying the transport properties of Cd_3As_2 thin films under certain configurations of magnetic and electric fields. The issue on the observed effect of the hole carrier predominance over electronic carriers in a number of investigated composites, the occurrence of which is most basically caused by processes in the Cd_3As_2 matrix and considering that the sample studied under the pressures up to 50 GPa is 10-30 μm in thickness, requires further experimental and theoretical investigations. All materials manifest peculiarities in the thermo-emf behavior (extrema, inflection points on the S(P) curves or pressure hysteresis) in the range of 28-35 GPa for $n=10$ and $n=20$, in the interval of 20-35 GPa for $n=30$, and in the interval of 30-35 GPa for $n=44.7$. The thermal-emf changes slightly or practically remains the same, when the pressure exceeds 40 GPa, both at increasing and subsequent decreasing pressures.

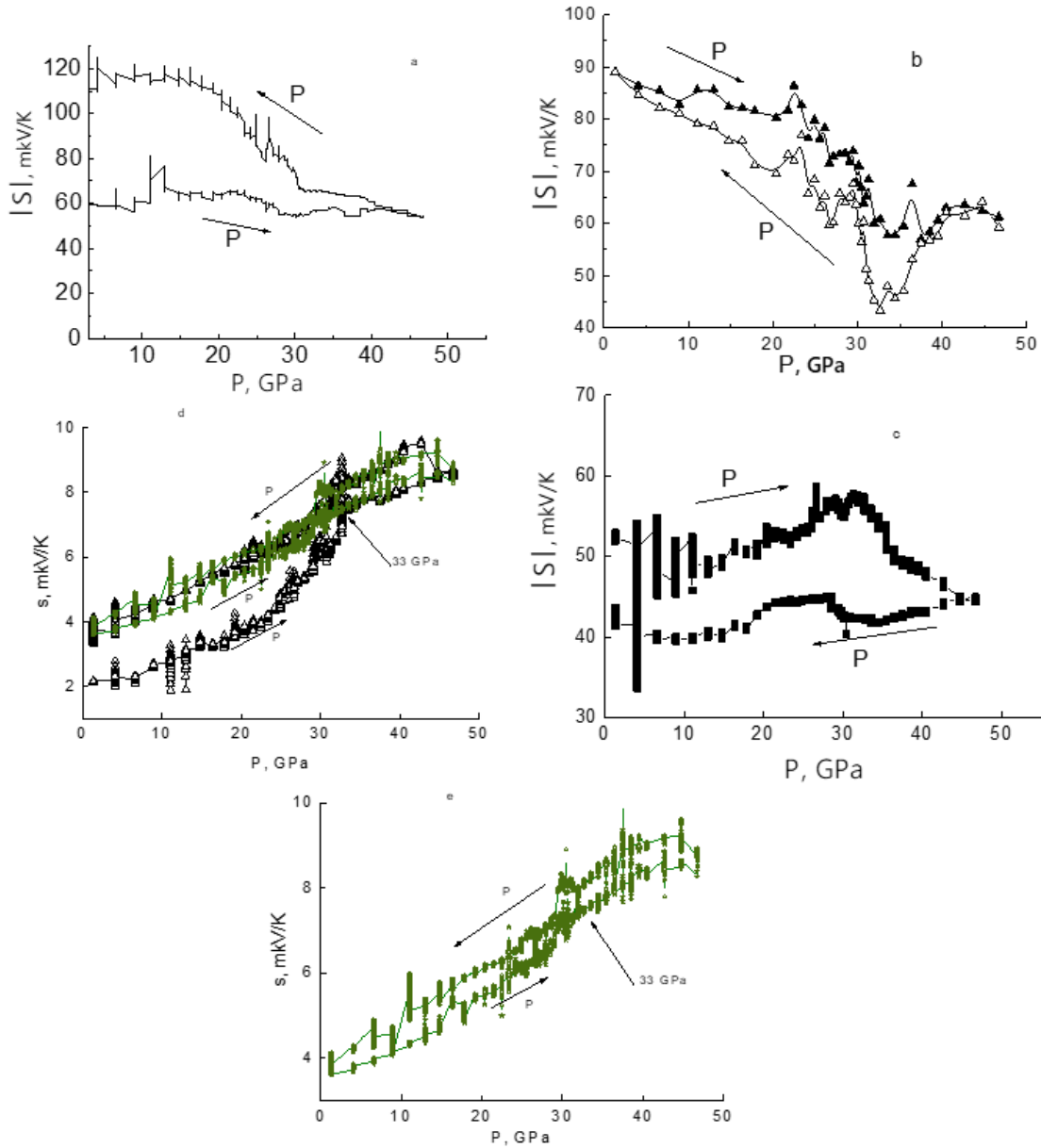


Fig. 4. Dependences of the Seebeck coefficient on monotonically increasing and decreasing pressure of composites a) $\text{Cd}_3\text{As}_2 + 10\%$ mol. MnAs, b) $\text{Cd}_3\text{As}_2 + 20\%$ mol. MnAs, c) $\text{Cd}_3\text{As}_2 + 30\%$ mol. MnAs; d, e) $\text{Cd}_3\text{As}_2 + 44.7\%$ mol. MnAs.

Note that Figure 4. (c) depicts features as inflection points in the pressure range of 20-35 GPa. The samples with other amounts of MnAs (see Figure 4. a, b) also show similar changes in this pressure range. This behavior can be explained by a structural or electronic phase transition occurring in this pressure range.

When high hydrostatic pressure is applied and the system is placed in an electric field, the relaxation of the nonequilibrium system and a gradual transition to the equilibrium state will be observed. Relaxation processes of thermo-emf are well described (correlation coefficient ~ 0.97) by the exponential dependence (see Figure 5)

$$S = S_0 + A \cdot \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

where τ is the constant equal to the relaxation time, t is the time.

The experimental results show that an increase in relaxation time is registered in the range of 30-33 GPa in $\text{Cd}_3\text{As}_2 + n$ mol% MnAs composites, which is associated with a possible structural or electronic phase transition. As an example, Fig. 5 shows the $S(t)$ dependences for the composite $\text{Cd}_3\text{As}_2 + 30\%$ mol. MnAs. The negative sign of the thermo-emf (Fig. 5) corresponds to hole carriers at the appropriate

connection scheme of the devices to the employed setup described in [12].

The relaxation time of a thermo-emf constant value in the pressure range from 4 to 30 GPa is extremely short (a few seconds). And then, with further increase in pressure, it grows and remains at the level of 14-32 sec. up to approximately 42 GPa, then reduces to small again.

In the case of Cd₃As₂ + 44.7% mol. MnAs, the maximum values of the electrical resistance relaxation time are seen in the range of 30-33 GPa (see Figure 6).

When estimating the relaxation times of thermo-emf under pressure, the time dependences of thermo-emf at fixed pressure are better approximated by the first order exponent $S(t)=Ae^{-t/t_0}$. When attempting to approximate $S(t)$ by a double exponent, the two times coincide. It can be assumed that the shorter time $t_{\min}=\min\{t_1,t_2\}$, estimated from the time dependences of electrical resistance $R(t)=A_1e^{-t/t_1}+A_2e^{-t/t_2}$, corresponds to relaxation processes associated with changes in the width of the forbidden band and carrier concentration, while the longer time is associated with relaxation processes of the crystal lattice.

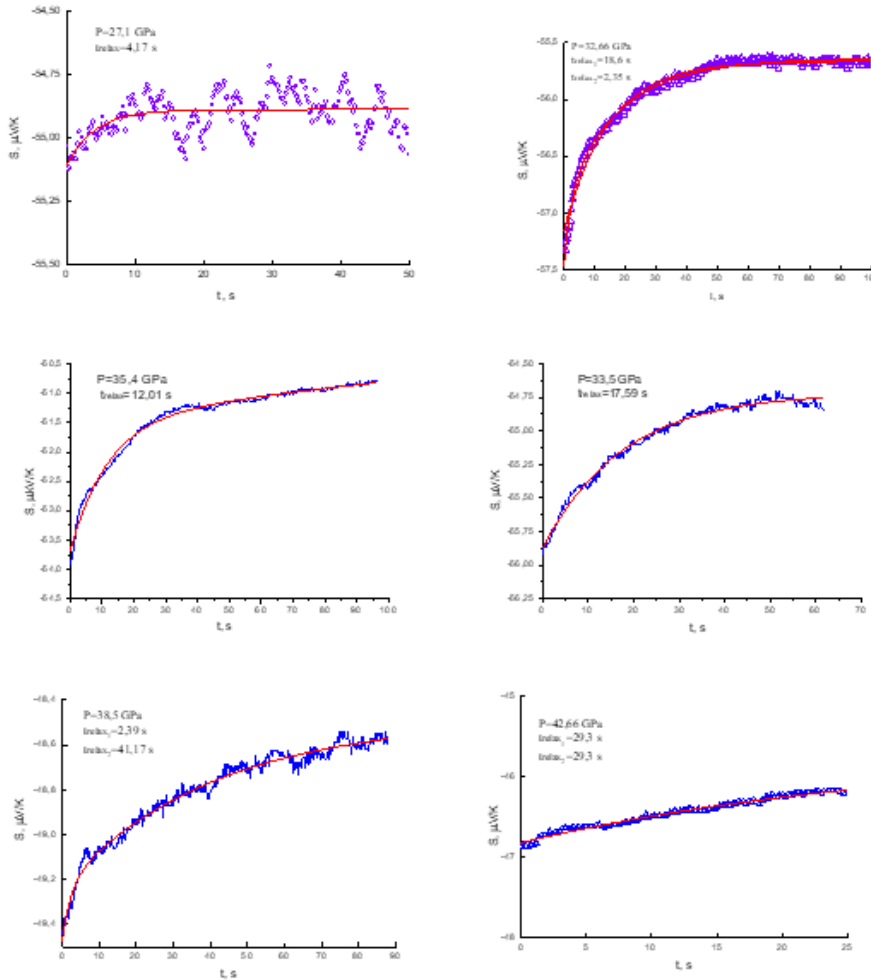


Fig. 5. Dependences of the Seebeck coefficient on the pressure holding time at the given pressure values for the Cd₃As₂ + 30% mol. MnAs composite.

This assumption is confirmed by the following: the change of thermo-emf with time, when holding the sample under a certain pressure, is characterized by a single relaxation time; at pressures above 23 GPa it is close, and at pressures 33 GPa and above it practically coincides (5-8 sec) with the smallest t_{\min} of the two estimated times from the approximation of the relaxation curve for the electrical resistance (Figure 6. b). The Cd₃As₂ + 44.7 mol. % MnAs structure, as mentioned above, is characterized by the electronic type of carriers, and the relaxation of the resistivity at high pressure is associated with charge transfer mechanisms such as electron tunneling between

ferromagnetic granules through the semiconductor barrier and possibly with hopping conduction by localized states.

Thus, summarizing the results of the study for all Cd₃As₂ + n mol% MnAs composites, we can conclude that features of thermal-emf dependences on the pressure are observed in the range of 28-35 GPa, and a significant increase in the relaxation time of the electrical resistivity and in a number of composites the relaxation time of the thermal-emf, associated with a possible structural or electronic phase transition, is found in the range of 30-33 GPa.

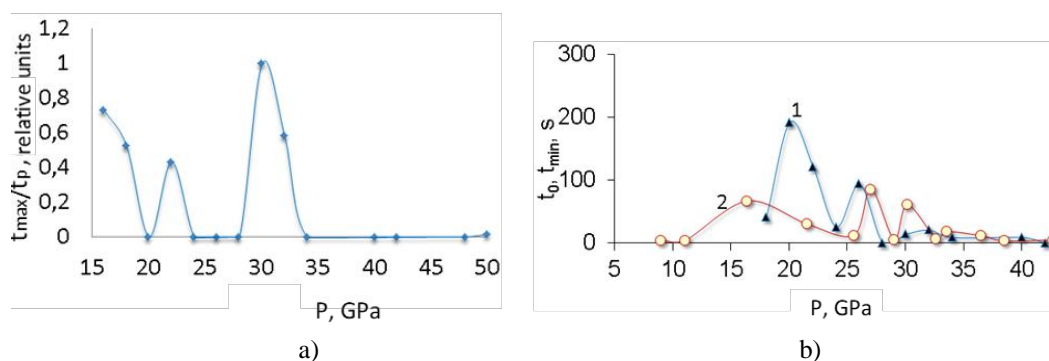


Fig. 6. a) Baric dependence of the relative value of the electrical resistance relaxation time t_{\max}/t_p , where t_{\max} is estimated from the approximation of the electrical resistance dependence on the time $R(t)=A_1e^{-t/t_1}+A_2e^{-t/t_2}$ at each fixed pressure as $t_{\max}=\max\{t_1,t_2\}$ and t_p is the largest of the experimentally estimated t_{\max} at 31 GPa; b) Baric dependences of the electrical resistance relaxation time $t_{\min}=\min\{t_1,t_2\}$, estimated from time dependences of electrical resistance $R(t)=A_1e^{-t/t_1}+A_2e^{-t/t_2}$ (curve 1), and the thermo-emf relaxation time t_0 , estimated from time dependences of thermo-emf $S(t)=Ae^{-t/t_0}$ (curve 2) for $\text{Cd}_3\text{As}_2 + 44.7 \text{ mol. \% MnAs}$ composite .

CONCLUSION

The specific features of the pressure-dependent behavior of the Seebeck coefficient are found for all considered $\text{Cd}_3\text{As}_2 + n \text{ mol. \% MnAs}$ composites in the range of 28-35 GPa. The data of relaxation processes at pressures up to 50 GPa prove that in the interval of 32-42 GPa in $\text{Cd}_3\text{As}_2 + n \text{ mol. \% MnAs}$ composites there is an increase in times of the relaxation, thermal-emf, and electrical resistance associated with a possible structural or electronic phase transition.

In view of the fact that the peculiarities of the pressure dependences of the relaxation, electrical resistivity, and thermo-emf times are primarily caused by changes in the characteristics of the electron subsystem of Cd_3As_2 , and the fact that the monoclinic crystalline phase of Cd_3As_2 is stable up to 50 GPa [16], as well as the fact that the distance apart the ferromagnetic nanogranules, between which electrons are tunneling in the composite, decreases with increase in pressure, we can conclude that the most probable transformations in the range of 30-35 GPa are the transformations in the electronic subsystem.

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