A new line in investigation of physical properties of rocks and minerals at high pressures and temperatures

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Abstract. The decisive problems at present in the experimental investigation of rocks and minerals at high pressures and temperatures are the problems of studying processes which are going on inside using various physical methods. The most important avenue of experiments is investigation of changes of physical properties of the rocks and minerals at high pressures and temperatures. The majority of papers in this line give a quantitative assessment of the physical characteristics, establish factors these characteristics depend on, and major patterns of their variation at high pressure and temperature parameters. Aside of this, abnormal manifestations of physical properties of the rocks were revealed prior to destruction, in the dehydration processes and in the phase changes [*Levykin,* 1991; *Parkhomenko,* 2000; *Volarovich et al.,* 1974, 1975, 1979a]. These investigations suggested that the abnormal changes of the rock physical parameters at high pressures and temperatures indicate to one or another process and are connected with the microstructure changes in the rocks and minerals. With allowance for the main direction, problems were set before the laboratory working on simulation and analysis of processes in the seismic zones to investigate a physical nature of the earthquake preparation processes and the attendant forerunners, at different scale levels, on the basis of experimental investigations of the rock and mineral properties and their variation at high pressures and temperatures. The neutron diffraction method, as the method possessing optimum capabilities among other microstructure methods of investigation of the matter, was selected as a physical investigation method. Calcite, that have received the most study at high pressure and temperature parameters and which is prevailing in the Earth, was selected as the first object of investigation.

First, we have made a set of tests on the calcite containing rock – marble of different graininess, with the purpose of assessing capability of the neutron diffraction method for investigation of processes in the rocks. It is well known that reversible polymorphous transitions take place in the marble, and it should be noted that these are observed under certain loading conditions, while they are not observed under other loading conditions. Therefore, the marble samples were tested under different loading conditions. The tests

were made on a solid phase cylinder-piston machine up to 1.6 GPa and on a high-pressure hydraulic machine at a constant hydrostatic pressure 10 MPa with an additional uniaxial compression at a speed of 1.8×10^{-6} mm/s [*Efimova et al.,* 1998]. At the beginning reading was made of the neutron diffraction spectra on each sample and complete pole figures were obtained showing orientation of grains in the sample under investigation in corpore and not in one plane, as a conventional microscopy allows to have. Afterwards, the samples were subjected to different loading conditions and new spectra were recorded after the tests and new pole figures were obtained. The neutron diffraction measurements were made in the UINI (Dubna), on the NSVR spectrometer, sheaf no. 7 of the IBR-2 reactor. A time-of-flight neutron diffraction method was employed for the textural measurements. Two transitions at 0.4 MPa and at 1.6 MPa were
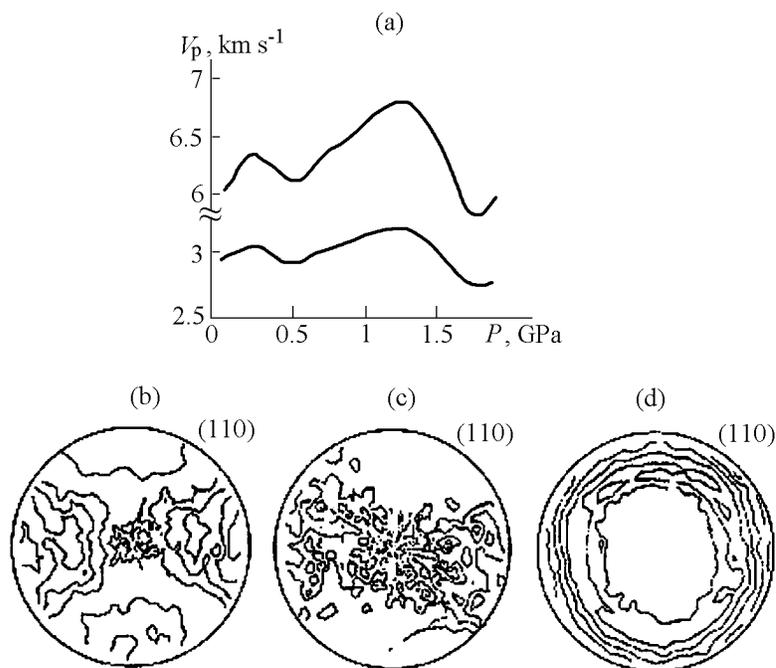
Figure 1. Pressure-elastic wave velocity curves for fine-grained marble (a) and its attenuation (b), as well as the pole figures of the sample in plane (110) (crystal-physical indices) before the test (c), after the first loading up to 0.6 GPa (d) and after loading up to 1.6 GPa.

found by the impulse ultrasonic method during deformation of marble under a quasihydrostatic pressure.

The texture analysis, made with the use of the neutron diffraction method on the NSVR diffractometer, has shown that the texture shape changes and rotates at the first and at the second transitions and a new metastable structural modification of calcite appeared having a distinct block structure. The oriented elements of the new phase are arranged locally at those points where microstresses were retained (Figure 1). The results obtained were supported by an X-ray structure analysis that was done by M. G. Zilbershmidt on the samples before and after experiment. Experiments on the marble under a constant hydrostatic pressure of 10 MPa with an additional axial compression have shown that the phase transition process is accompanied by a reduction of the deformation characteristics of a sample. Figure 2 shows the pole figures of this sample in plane (001) before and after the test. As is seen from the pole figures, the internal structure of the sample, which had originally a large-block structure, has decompressed as a result of the phase transition. The isolines on the pole figures show exposures of the calcite crystallites in the sample. The texture analysis has shown that an off-orientation of the block structure of the sample takes place during the transition. This off-orientation is a consequence of relaxation. The off-orientation degree is an index of the process intensity. Results in the last experiment were confirmed by investigations of sections of the samples made on an electron microscope before and after the experiment. The samples grew dull after the experiment, a strong fine cracking occurred inside the sample thus testifying a poly-

morphous transition which has taken place, similar to that observed in the calcite monocrystal at the triaxial compression [*Volarovich et al.,* 1975, 1979b]. The results obtained suggest that processes are likely to take place in the Earth's crust, which are accompanied both by the off-orientation of the block structure and its enlargement. This experiment is a further proof of conclusions of our previous work about the interrelation of processes which take place at different scale levels [*Sobolev et al.,* 1995]. Thus, it was determined that the neutron diffraction method is reasonably informative for studying processes which are going on in the rocks and in
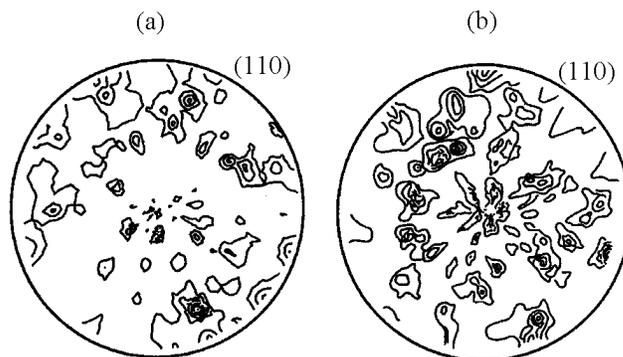

Figure 2. Pole figures of coarse-grain marble in plane (110) (crystal-physical indices): 1 – before the test, 2 – after the test.

the minerals at high pressures and temperatures.

A team of research fellows from the IPHP, IPE RAS and UINI has developed an apparatus/measuring complex with a VME computer-based automated control system of the experiment in a neutron beam, with data acquisition and processing. No analogues are available in the world. A high-temperature uniaxial compression machine with a pickup system is one of the most important components of this complex (Figure 3). Parameters of the machine are as follows: the uniaxial compression force is 1.5×10^4 H, the sample volume is up to 10 cm^3, temperature is up to 600°C. The design of the machine presents a possibility of modifying the loading parameters on the run in the neutron beam directly and recording the neutron spectra, which carry information about structural changes of the lattices, and a structural analysis at any stage of the experiment. Chamber of the new machine, which is transparent for the neutrons, is made of a titanium-zirconium alloy [*Efimova et al.,* 1997]. Figure 4 shows two diffraction spectra. The first, with high-intensity reflexes, is recorded from a chamber at a room temperature, the second one from a chamber containing the sample. Since the sample consisted dominantly of calcite, the spectra contain the indexing peaks of calcite. A theoretical calcite spectrum calculated on the basis of structural parameters of calcite and the Bragg diffraction law was used for indexing the calcite spectra. It is well seen that the calcite peaks are not covered by peals which belong to the chamber. Figure 5 shows arrangement of the measuring elements: piezosensors for emission and reception of ultrasound, tensometers, thermocouples and a heater (for the first version of the machine). The sample was heated at a constant rate of 2°C/min. The experimental/measuring complex and a procedure of a simultaneous measurement of the elastic, deformation, structural and texture characteristics of the rocks and minerals in the neutron beam at high pressure and temperature, makes it possible to carry out a continuous recording and a quantitative assessment at the microstructure level of physical parameters of the rocks and other materials of a natural and artificial origin in the course of their variation and analyze them by employing the texture analysis method. [*Efimova et al.,* 1997; *Ivankina et al.,* 1999; *Kireenkova and Efimova,* 2000].

Two cylindrical marble samples (Sn3d – Sn4d) of 16 mm in diameter and 20 mm long were considered. A prevailing orientation of the calcite grains was measured in the beginning of the tests at a room temperature, i.e. texture of the samples was measured. Afterwards the sample was placed in a high-temperature machine, which was installed in its turn in a SKAT texture diffractometer. The machine is secured in a ring of the SKAT and rotates together with it. The SKAT is essentially a ring 2 m in diameter with 19 detectors mounted thereon. The detector system is arranged axially symmetric to the neutron beam and the angle of deflection for all detectors is equal to 90° [*Ivankina et al.,* 2001]. Thereafter the samples were subjected to a uniaxial compression at 13 and 20 MPa accordingly. The mechanical stress was increasing by 100% and 60% along with the increase of temperature.

In the course of tests temperature first increased from the room temperature up to 50°C at the rate of 2°C per minute
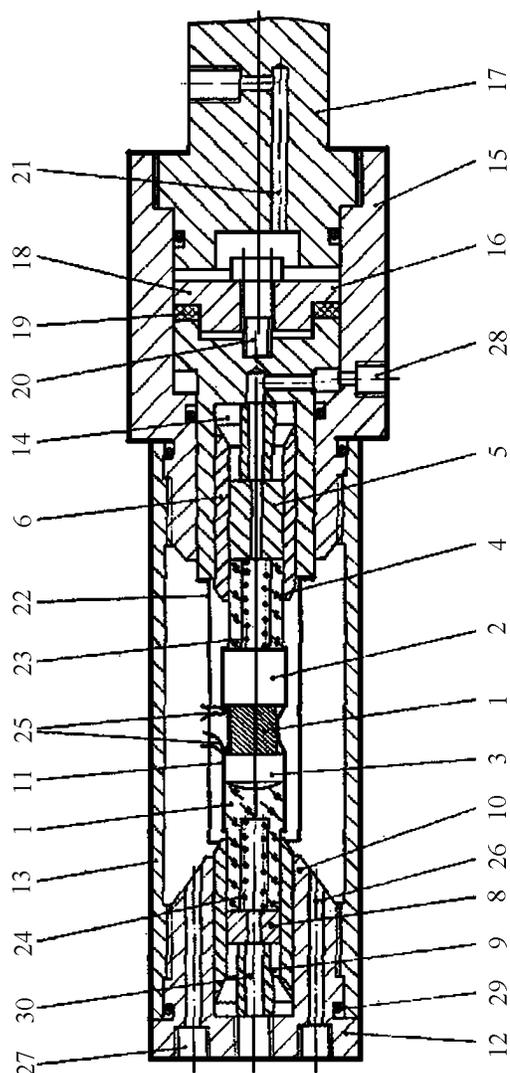

Figure 3. Thermal-controlled uniaxial compression chamber: 1 – sample; 2, 3, 4 – sapphire support, trunnion ball (sapphire), sapphire bush; 5, 8 – hard-alloy bushes; 6, 10 – high-temperature steel bushes; 7 – sapphire barrel; 9, 14 – relief gaskets; 11 – centering collet; 12 – plug; 13 – casing; 15 – hydraulic cylinder; 16 – piston; 17 – shaft; 18 – adjusting button; 19 – packing ring; 20 – bolt; 21 – oil valve; 22 – shield; 23, 24 – heaters; 25 – thermocouples; 26 – vacuum exhaust channel; 27 – thermocouple lead-in; 28, 30 – power points; 29 – packing ring.

and then temperature was stabilizing for 10 minutes and after this the neutron diffraction was recorded by all the detectors of the SKAT spectrometer for an hour. Similar cycles were repeated several times at 30–40°C temperature intervals. The time of the ultrasonic pulses going through the samples and parameters of the sample were recorded continuously.

In case of sample Sn3d spectra were recorded for six temperature points (temperature rise, stabilization of temperature, measurement of diffraction at a constant temperature)
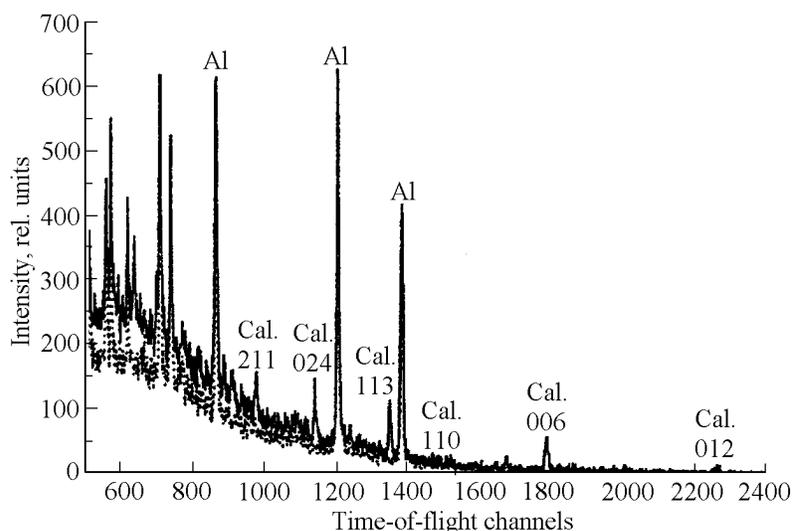
Figure 4. Diffraction spectra recorded from the chamber without the sample (dotted line); from the chamber with the marble sample (solid line).
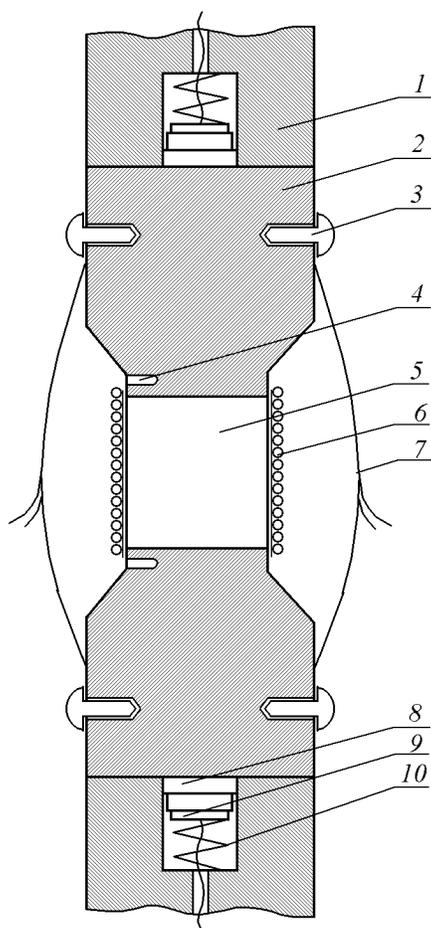

Figure 5. Assembly of the TKOS measuring system: 1 – bearings; 2 – anvils; 3 – fixing bolts for cramps with strain sensors; 4 – thermocouple pockets; 5 – sample; 6 – heater; 7 – strain sensors on deformation cramps; 8 – ultrasonic sensors; 9 – connections with high-frequency cable; 10 – spring.

and in the case of sample Sn4d spectra were recorded for five temperature values.

A prevailing orientation of grains (texture) of the samples was measured at the beginning of the test at a room temperature. Afterwards measurement of texture in sample Sn3d was made at $220°C$ and in sample Sn4d at $250°C$. After the measurement of the sample Sn4d texture made at $250°C$, the uniaxial stress at the ends of the sample was increased up to 110 MPa by pumping a press and with this mechanical stress the diffraction spectra were also recorded. At a reverse temperature reduction the diffraction was measured at $50°C$. The texture measurements of sample Sn3d have taken of 3400 minutes of net time, the exposure time for sample Sn4d during the texture measurement was increased and the whole experiment lasted for 7800 minutes. The diffraction spectra were recorded during one hour at the temperature and stress values reached. No changes were observed whatsoever. This suggests that a fast increase of the uniaxial compression did not cause any change of the texture. Subsequently the texture of sample Sn4d was measured once again after it was kept under load for a long time (140 days) in a chamber (TKOS). The stress has reduced down to 10 MPa during this period and this can be attributed to the stress relaxation and to the creep flow in the marble and also to relaxation of the pressure transferring medium. The diffraction spectra of sample Sn3d were also repeatedly measured, but in this case only subject to the temperature impact (at the same temperature points) and without any mechanical compression.

The temperature effect resulted in insignificant changes of the sample Sn3d texture. Of some interest is a comparison of the pole figures of sample Sn4d, characterizing texture at the maximum temperature $(250°C)$ with the pole figures of the same sample after a long period when it was kept under the load. The pole figures, measured on the sample after a long mechanical stress, have shown that the structure was changed towards a greater order of the plane orientation (11–20) (Figure 6).
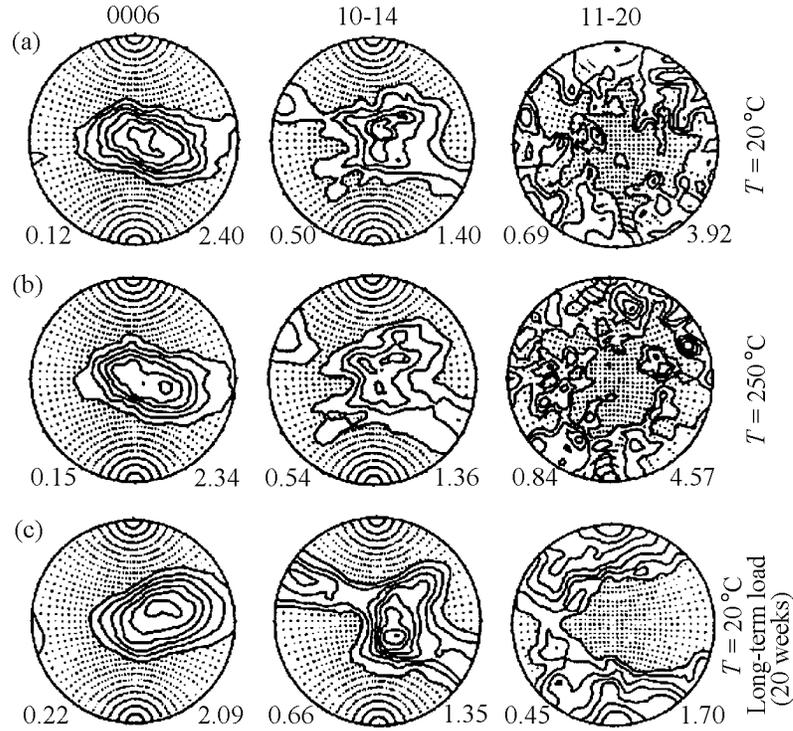
Figure 6. Pole figures of Sn4d marble sample, measured (a) – at $20°$C; (b) – at $250°$C; (c) – after a long-term load (140 days).

Influence of temperature for both samples became apparent in displacement of the peaks, most characteristic for the theoretical diffraction spectrum of calcite. However the displacement is not great for all the peaks. The maximum displacement is observed in the peak (0006). It amounts to 1.79×10^{-2} Å in the temperature interval 20–$190°$C, that corresponds to a linear relative deformation ($\Delta d/d_0 = 6.20 \times 10^{-3}$). Thus, the change of position of the time-of-flight diffraction spectra peaks may help to determine the change of the interatomic distances in the calcite crystal lattice as the temperature increases [*Ivankina et al.,* 2001].

Comparison of the microdeformation values and thermal characteristics of calcite at different temperatures, obtained from the neutron diffraction data and calculated on the basis of the structural characteristics of calcite defined by an X-ray structure method [*Markgraf and Reeder,* 1985] has shown that the displacement values and relative deforma-

Table 1. Values of absolute and relative deformation of the calcite crystal lattice and coefficient of thermal expansion of sample Sn4d within a temperature interval from $20°$C up to $250°$C

| (hkil)	T$°$C	d, Å	Δd, Å	$\Delta d/d_0$	$\Delta d/d_0 \Delta T, [K^{-1}]$	δ, Å
(0006)	20	2.836731	–	–	–	2.70×10^{-4}
	120	2.845883	0.00915	3.23×10^{-3}	32.3×10^{-6}	1.93×10^{-4}
	180	2.853039	0.01631	5.74×10^{-3}	35.9×10^{-6}	1.69×10^{-4}
	220	2.856836	0.02011	7.09×10^{-3}	35.4×10^{-6}	1.21×10^{-4}
	250	2.860350	0.02362	8.33×10^{-3}	36.2×10^{-6}	1.83×10^{-4}
(11–20)	20	2.488342	–	–	–	3.07×10^{-4}
	120	2.488135	-0.00021	-0.08×10^{-3}	0.83×10^{-6}	1.71×10^{-4}
	180	2.487260	-0.00108	-0.43×10^{-3}	-2.72×10^{-6}	2.95×10^{-4}
	220	2.486819	-0.00152	-0.61×10^{-3}	-3.06×10^{-6}	2.33×10^{-4}
	250	2.486863	-0.00148	-0.59×10^{-3}	-2.58×10^{-6}	1.75×10^{-4}

Table 2. Values of absolute and relative deformation of the calcite crystal lattice and coefficient of thermal expansion of sample Sn3d within a temperature interval from 20°C up to 220°C

(hkil)	T°	d, Å	Δd, Å	$\Delta d/d_0$	$\Delta d/d_0\Delta t, [K^{-1}]$	δ, Å
(0006)	20	2.837580	–	–	–	1.74×10^{-4}
	50	2.839878	0.00230	0.81×10^{-3}	27.00×10^{-6}	3.77×10^{-4}
	80	2.843278	0.00570	2.00×10^{-3}	33.47×10^{-6}	4.44×10^{-4}
	120	2.848861	0.01128	3.98×10^{-3}	39.76×10^{-6}	3.00×10^{-4}
	150	2.852111	0.01453	5.12×10^{-3}	39.39×10^{-6}	4.20×10^{-4}
	190	2.855393	0.01781	6.28×10^{-3}	36.93×10^{-6}	7.86×10^{-4}
	220	2.858762	0.02118	7.46×10^{-3}	37.33×10^{-6}	3.90×10^{-4}
(11–20)	20	2.4897098	–	–	–	3.31×10^{-4}
	50	2.489688	-0.00011	-0.04×10^{-3}	-1.47×10^{-6}	3.25×10^{-4}
	80	2.489185	-0.00061	-0.25×10^{-3}	-4.10×10^{-6}	3.73×10^{-4}
	120	2.488685	0.00111	-0.45×10^{-3}	4.47×10^{-6}	3.42×10^{-4}
	150	2.487876	-0.00192	-0.77×10^{-3}	5.94×10^{-6}	4.85×10^{-4}
	190	2.487399	-0.00250	-1.00×10^{-3}	-5.90×10^{-6}	5.14×10^{-4}
	220	2.484689	-0.00267	-1.07×10^{-3}	-5.35×10^{-6}	6.32×10^{-4}

Notes to tables 1 and 2: d – distance between atomic planes described by the Miller indices hkil of the calcite crystal lattice; $\Delta d/d_0$ – linear relative deformation; δ (Å) – error in determination of the peak on the diffraction spectrum; d_0 – interplanar spacing at a room temperature; T° – temperature in °C; $\Delta d = d - d_0$ – deformation of the calcite crystal lattice under temperature; $\Delta d/d_0\Delta T, [K^{-1}]$ – linear thermal expansion coefficient.

tions in our experiments exceed similar values obtained from data of the X-ray structure analysis on the calcite monocrystal. Different conditions of the experiment may be one of the reasons of this discrepancy. The neutron diffraction experiments were conducted at a simultaneous impact of both temperature and the uniaxial compression, while in the work of [*Markgraf and Reeder,* 1985] measurements were made subject to temperature only.

The temperature experiment on recording the neutron
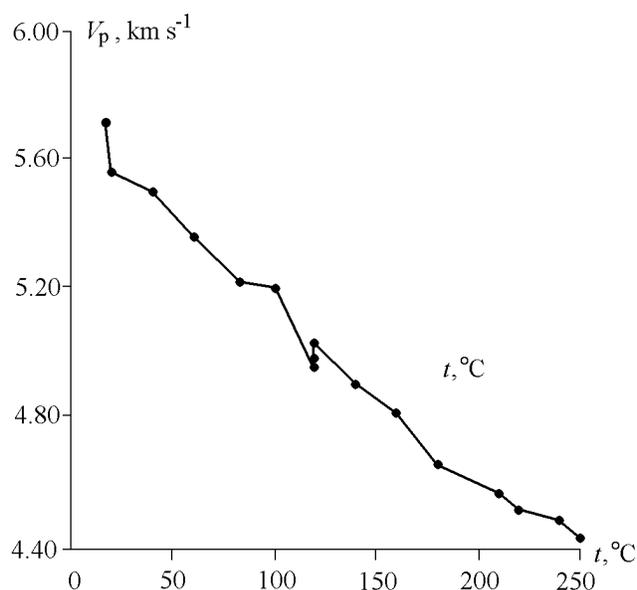
Figure 7. Temperature dependence of the longitudinal wave velocity in the direction of the center line of the marble cylindrical sample.

diffraction spectra under the same temperatures with sample Sn3d, where no texture changes were observed, as was mentioned earlier, was conducted just with the aim of comparison. The results of this experiment, however, have proved that deformations in the plane (0006) as a result of the thermal expansion under all temperature values were higher than in the case of a simultaneous action of the uniaxial compression and temperature. The deformation values of plane (11–20) in two experiments at 120°C and 220°C (Tables 1 and 2) are very close to each other. This speaks about a very weak sensitivity of the lattice in this direction to a mechanical effect. As can be seen from Tables 1 and 2, the calcite thermal expansion coefficient has different values and signs in different planes, i.e. anisotropy of the calcite thermal expansion coefficient is observed. This fact belongs also to the carbonate-otavite, while other carbonates have only positive thermal expansion coefficients. Changes of the thermal expansion components for different crystallographic directions (11–20) (0006) are just of an opposite nature. Thus, the temperature dependence of the thermal expansion components for plane (11–20) has a tendency to a reduction with the rise of temperature, whereas it increases for plane (0006) along with the rise of temperature. A type of the temperature dependence of the thermal expansion coefficient has been also found for other directions in calcite.

The longitudinal wave velocities, propagating along the center line of samples, were measure by an ultrasonic pulse method [*Kireenkova and Safarov,* 1979; *Volarovich et al.,* 1974, 1975]. A temperature dependence of the longitudinal wave velocity for sample Sn3d (Figure 7) is shown as an example. Piezoradiators with a calibrated frequency 1 MHz are made of piezoceramics CTS-26 and they are designed for a continuous duty at a temperature up to 350°C. A temperature dependant elastic constant $c_{33} = \rho V^2$ was found on the basis of data about the longitudinal wave propaga-

tion velocity and a calculated density. The data obtained were compared with the data taken from the reference book [*Single...,* 1971]. It was shown that the $c_{33} = f(T)$ curves obtained by us and taken from references are parallel with each other. Apparently the values will become more close when corrections for variation of the sample length will be introduced.

As a result of the first experiments with the use of a complex of physical methods, ultrasonic pulse method and the neutron diffraction method the physical, structural and texture characteristics of the rock were recorded and a quantitative assessment was made in the course of its deformation at high pressure and temperature parameters. This suggests that the new line in investigation of the physical properties of the rocks and minerals at high pressures and temperatures is promising for the study of the deformation processes in lithosphere.

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