

Electrical and Thermal Investigations of Rocks and Minerals under Extreme p , T -Conditions¹⁾

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Summary – For the discussion of the physico-chemical state and the phase transitions in the earth interior it is necessary to compare the results of geophysical field measurements with geophysical solid state investigations in the laboratory under extreme p , T -conditions. In correspondence with the theoretical studies about the behaviour of the materials in the deep earth we investigated two groups of materials: (I) different types of rocks with reference to their elastic and thermal behaviour under extreme conditions, (II) simple compounds of elements which belong possibly to the representatives of the deep mantle and the earth interior. The method for measurement of the thermal diffusivity and the influence of anisotropy on the propagation of elastic waves in different rocks is described. The results of the dependence of the electric resistivity on pressure and temperature on synthetic and natural chalcogenides of the $3d$ -transition metals are discussed.

1. Introduction

Recently it has turned out more and more clearly that laboratory experiments under extreme pressure and temperature conditions are inevitable for a successful interpretation of geophysical models of the earth's crust or deeper parts. This applies to petrological investigations in the same way as to studies of the structure of the deeper earth's interior, here especially in connection with seismological investigations as well as theoretical work for deriving adequate equations of state (STILLER *et al.*, 1974, 1975; VOLLSTÄDT *et al.*, 1974).

2. Measurement of thermal parameters

The knowledge of heat conductivity is of particular importance. When using the temperature data obtained from deep borings, the question arises as to whether it is still possible to calculate with the heat conductivity values determined from bore cores under normal conditions in the laboratory. It can be expected that the thermal parameters are subject to substantial changes in the course of sampling and due to the

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subsequent sample preparation (loosening of grain contacts, crack initiation). By applying a high pressure, these changes should be largely removed and the original state characterized by the conditions of great depth should be simulated. Such determinations of heat conductivity under high pressure were hardly undertaken up to now. Indeed, it was already in 1924 when a beginning was made by Bridgman carrying out an investigation of 5 different rocks; but afterwards the development remained largely stagnant. The experiments carried out at that time used a stationary measuring technique which required a highly precise preparation of a sample being rather complicated for rocks.

When measuring heat conductivity in a high-pressure chamber, generally a number of decisive limitations has to be taken into account. The requirement that the setup should occupy a small space, and the close contact between the sample and the pressure-transmitting medium exclude the possibility of thermal insulation. Thus techniques using samples which are approximately one-dimensional in extension cannot be realized. The most convenient measuring techniques should be those using cylindrical samples, particularly if the experimental conditions can be selected so as to permit assuming the extension in axial direction to be infinitely large, so that it is possible to eliminate the dependence of the temperature distribution on the z -coordinate by introducing cylindrical coordinates (SEIPOLD and GUTZEIT, 1975). According to the problem given a special design of the pressure chamber was developed (Fig. 1). The cylindrical sample is enclosed by a tubular heating element made of resistance sheet material, which is fed by a periodically varying heating current. This causes temperature waves to develop in the sample. The amplitude of these waves is measured by means of thermo-couples in the cylinder axis ($r = 0$) and at its surface ($r = R$). As most of the nonstationary methods do, this method yields the thermal diffusivity K , which is, however, closely related to thermal conductivity by the relation

$$\lambda = c\rho K.$$

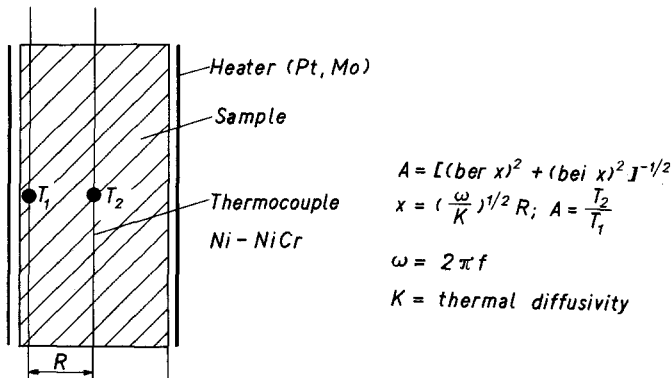


Figure 1
Principle of the measurement of heat conductivity under high pressure conditions.

Among the quantities occurring in this equation, the thermal capacity c , due to its physical causes, is nearly invariable within the pressure range considered. The pressure dependence of density ρ is accessible by measurement, so that, for known values of K , also the heat conductivity is in effect determined.

The measurements were carried out in an oil-pressure chamber according to the piston-cylinder principle under hydrostatic conditions. The samples used in the measurements were air-dry. They were coated with a surface coating in order to prevent oil from penetrating into the pores. Several materials were tested for performing this sealing function, e.g. water glass and organic adhesives diluted with acetone. It was found that they had no effect on the results. Also for cementing the thermo-couples into the samples slots, we tested various substances, since in principle there is a possibility of a thermal short circuit to occur when a material of high thermal conductivity is used. Experiments with fine-grained powders of MgO and Al_2O_3 and stone dust of different grain sizes were carried out, the cements used being in most cases water glass or also organic adhesives. We did not find any significant effect on the measured values.

It was generally expected that the heat conductivity of rocks would show a pressure dependence similar to that of the sound-wave velocities, i.e. that within the range of several kilobar a considerable increase would occur which would then gradually change over into a slower linear increase. In investigations with uniaxial load by HURTIG and BRUGGER (1970) such a behaviour had been found to occur, which can be made quite plausible by considering the action of macroscopic effects such as the closing of pores and cracks at low pressures. On the other hand, the measurements performed by BRIDGMAN (1924) at five different rocks showed only rather weak pressure dependencies (0.1 to 3.6% kb) and a linear relationship. Our own investigations led to similar results. Though particularly the range of low pressures was most thoroughly investigated, only slight variations of thermal diffusivity were found in the range up to 3 kb for the rocks considered (various sandstones, granite, anhydrite). For the sandstone samples and the granite, it was possible to describe the dependence by a linear relation of the following form:

$$K = K_0(1 + ap). \quad (1)$$

For the relative increase of thermal diffusivity

$$a = \frac{\Delta K}{K_0} \cdot \frac{1}{p} \quad (2)$$

the following values were found:

Sandstone, sample 1:	$a = 2.2 \cdot 10^{-2}$ kb
Sandstone, sample 25:	$a = 0.5 \cdot 10^{-2}$ kb
Sandstone, sample 60:	$a = 1.7 \cdot 10^{-2}$ kb
Granite:	$a = 4.4 \cdot 10^{-2}$ kb.

These values are of the same order of magnitude as the increase measured by STAUDACHER (1973) for olivine in the range up to 20 kb (appr. $1 \cdot 10^{-2}$ kb). This is most remarkable because the investigations of olivine were carried out under quite different experimental conditions. In the latter experiments, a much smaller sample was made by sintering from a powdery starting material and measured in a quasi-hydrostatic pressure chamber. The results show that, in contrast to the situation with the sound-velocity measurements, in the case of the pressure dependence of thermal diffusivity it is not possible to separate the macroscopically caused pressure effects from the microscopically caused ones.

The samples of anhydrite showed a somewhat irregular behaviour with a considerable hysteresis occurring between loading and relieving. In this case the thermal diffusivity in certain ranges even decreases with increasing pressure. It was examined whether anisotropies caused by stratification have any influence. To this end, sample cylinders were bored in directions perpendicular and parallel to the plane of stratification. The results show that there is a considerable anisotropy, whereas the character of pressure dependence in different directions shows only minor differences.

Altogether, it can be stated that in the considered pressure range up to 3 kb the variations of temperature conductivity which are caused by pressure variations do not appreciably exceed a value of 10%, so that the decrease of conductivity due to temperature effects will be dominant in the corresponding depth range of the earth.

3. Anisotropy of the elastic properties

On the investigation of the elastic properties of rocks the determination of the sound velocity is very important. There are many papers about these measurements (e.g. VOLAROVICH, 1973, CHRISTENSEN, 1971, 1974). Contrary to this situation only few authors are engaged in the anisotropy of the elastic properties and their variation under extreme p , T -conditions (VOLAROVICH *et al.*, 1971).

The preparation of the samples strongly influences the reliability of the measured anisotropy values. The experimental arrangements after PROS (1974) is optimal using a spherical sample which can be measured in any direction. Of course, the apparatus and the preparation is very complicated and applicable only for a low pressure range.

The investigations were carried out with cube-shaped samples under quasi-hydrostatic conditions. A triaxial press served for pressure generation. The press generated maximum pressures of 300 Mp in the horizontal directions and 600 Mp in the vertical direction. The pressure-transmitting medium used was pyrophyllite forming a liquidlike jacket around the rock sample. For determining the anisotropy, ultrasonic transmitters and receivers were inserted into the opposite pistons. This permitted simultaneous measurements to be carried out in three mutually perpendicular directions. This method is much more satisfactory than investigating several samples of different orientations. The test cubes were cut out of the rock material in

such a way that one of the cube faces was parallel to the stratification plane. For determining the velocity of longitudinal waves, the delay time of ultrasonic pulses was measured. The delay-time measurement was carried out using a cable detecting equipment having an error of 50 ns. Inductive distance sensing elements located between the pistons served for the determination of the distance to be travelled, which varied with changing pressure.

Till now, in the literature there is no quantity being consistently used as a measure of anisotropy. We shall call the ratio

$$k = \frac{V_{\max}}{V_{\min}}$$

the factor of anisotropy, using it as a quantitative measure. Till now, a number of rocks was investigated. Emphasis was laid on the measurements with pyrophyllite, since this material is used in many cases as a pressure-transmitting medium, so that an accurate knowledge of its properties is required. Although no preferred direction was observed macroscopically with this material, a considerable anisotropy was found by the elastic measurements to exist (Fig. 2). The factor of anisotropy decreases with increasing pressure, but isotropy is not yet reached at 14 kb.

There are two causes for the anisotropy of sound propagation in rocks: the rock sample may possess pores and cracks with their axes arranged in definite directions. On the other hand, the mineral grains in rocks may be distributed because of the origin

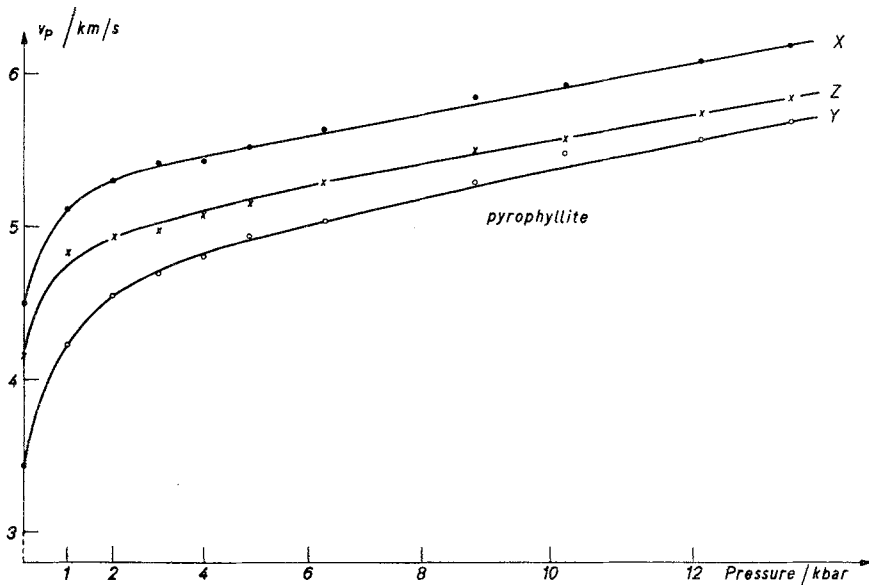


Figure 2

The pressure dependence of the longitudinal wave velocity in 3 directions for pyrophyllite up to 14 kbar.

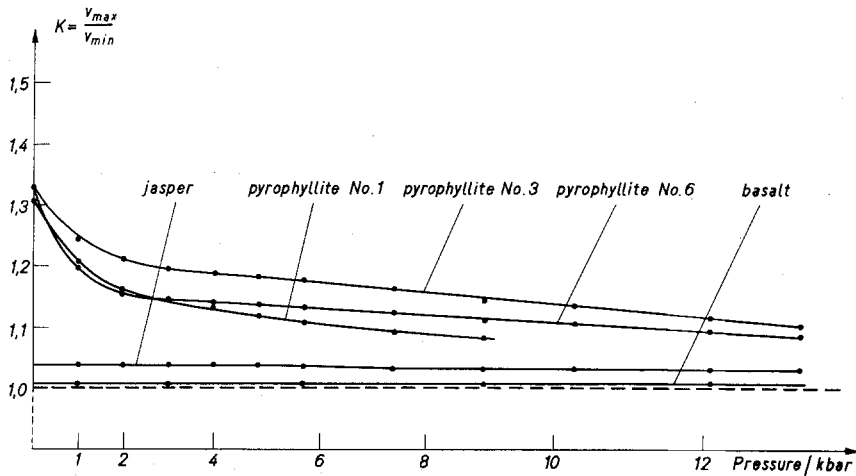


Figure 3

The different anisotropy behaviour under high pressure for some rocks and minerals.

conditions not statistically. We can expect that the anisotropy caused by the first possibility disappears with increasing pressure. In fact the investigations of pyrophyllite show a decrease of the anisotropy factor with pressure. Up to pressure of 14 kb an anisotropy remains. The reason can be the anisotropic shape of grains which will not be influenced by pressure. Therefore by using higher pressure it is possible to distinguish between the different causes of elastic anisotropy.

A complete other behaviour shows striped Jasper as a distinctly stratified material. It has a relatively low anisotropy ($k = 1.04$); moreover, this value hardly varies with changing pressure (Fig. 3). Samples of basalt and marble proved isotropic within the limits of measuring error.

4. Electrical conductivity investigations

Measurements of electrical conductivity were mainly carried out with minerals and synthetic compounds which are possibly of importance for the structure of the deeper earth's interior. The compounds concerned are the homologous of the 3d-transition metal sulfides (VOLLSTÄDT and SEIPOLD, 1974).

Relatively little was known about the properties of these compounds. The hitherto performed investigations concentrated upon the magnetic behaviour. Almost all of the compounds have a nickel-arsenide structure, the exceptions being manganese sulfide and selenide. Very little is known, too, about the behaviour under high pressures, and especially about the stability of the crystal structure (KJEKSHUS and PEARSON, 1964).

The investigations were carried out using a Bridgman apparatus. In this case the sample is placed in a flat ring made of an insulating material, such as pyrophyllite or Novomicanite (an artificial mica). The disk formed by the combination of sample and

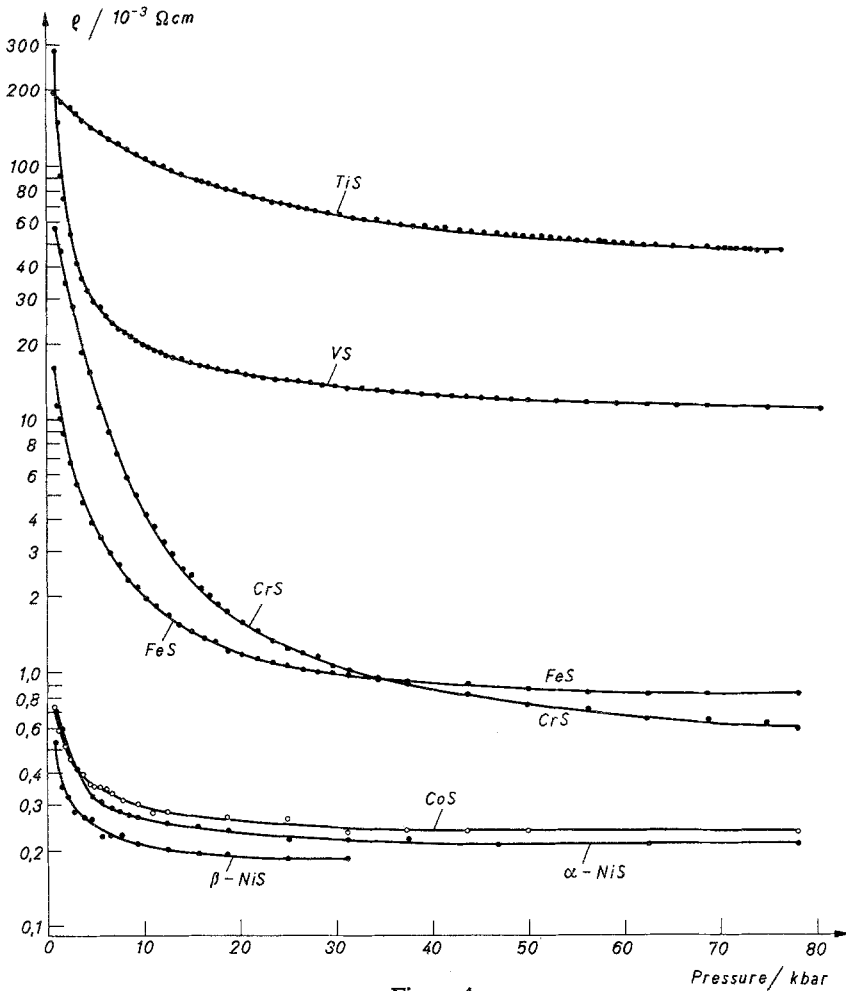


Figure 4

The pressure dependence of the specific resistivity of 3d-transition metal sulphides (without MnS).

ring is subjected to pressure between two pistons consisting of tungsten carbide. Heating is accomplished by means of an external oven enclosing the piston holders. The oven is made up of two sections, so that the sample chamber is readily accessible. By means of an asymmetrical arrangement of the oven sections it is possible to produce, if required, a temperature gradient within the sample. In the Bridgman squeezer, usually it is only possible to measure very flat samples. Since the substances investigated had very high conductances, problems arose due to the very low resistances (less than 0.1 milliohm). These problems were avoided by a special sample arrangement. The resistivity measurement was carried out using a Thomson bridge.

First of all, the pressure dependence of resistivity was measured at room temperature. It turned out that the specific resistivities decrease very rapidly with increasing pressure (Fig. 4). The final values are in part already very close to that of the metals.

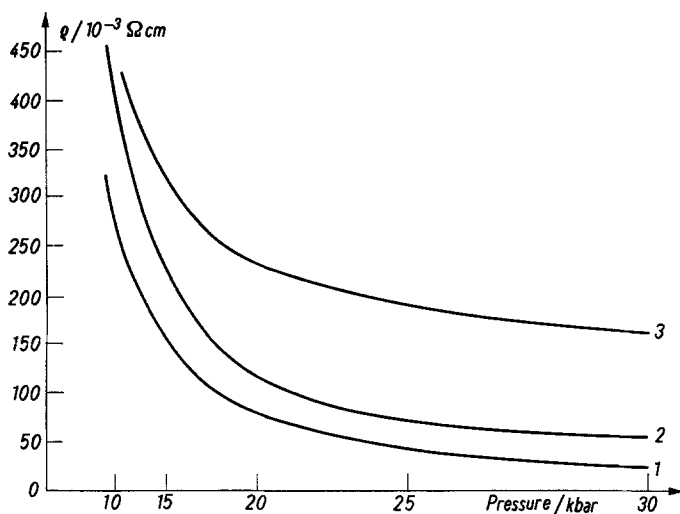


Figure 5

Specific resistivity ρ of different iron sulphides in dependence on pressure: (1) Troilite-meteorite from Dornbach/Rhön; (2) Troilite-meteorite from Georgia/USA 1870 (values multiplied by factor 10); (3) Synthetic FeS (values multiplied by factor 100).

This holds particularly for all cobalt and nickel compounds. In this case already at low pressures a high conductivity is reached, which does not appreciably vary when the pressure is further increased. Generally the resistivity decreases when passing from sulphides to selenides and then to tellurides. This corresponds to the general tendency of the metallic character to increase with increasing atomic number within a series of homologous elements.

The dependence of the electrical resistivity of natural and meteoritic iron sulphide is investigated too (see Fig. 5).

Generally the investigations of the temperature dependence of conductivity provide important information on the mechanism of conduction. Till now, in the case of chalcogenides these investigations were carried out for several selected substances. Fig. 6 shows the behaviour of iron sulphide. It is decisively determined by the occurrence of the so-called α -transition. The existence of the latter is already known from papers of other authors. It is seen that, with increasing pressure, the thermodynamic equilibrium is shifted in favour of the high-temperature phase. Already at 10 kb the low-temperature phase is no longer stable at room temperature. According to BERTAUT (1953) the high-temperature phase has the normal NiAs structure. The low-temperature phase is a superstructure with hexagonal symmetry. It develops from the nickel-arsenide structure by a slight displacement of the iron ions. The high pressure enforces the phase having the smaller elementary lattice cell. Because of the phase transition, no information about the type of conduction can be obtained from the temperature dependence of conductivity.

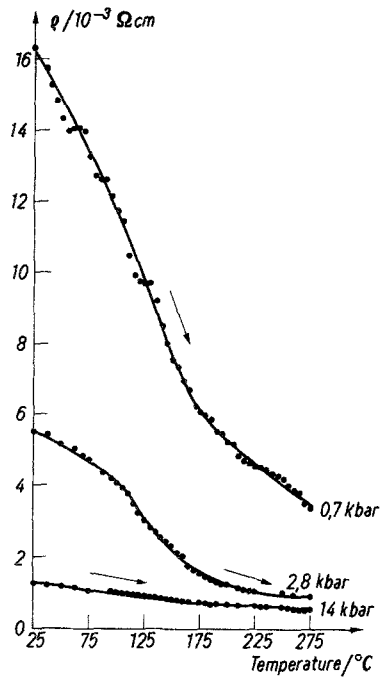


Figure 6
The influence of temperature on the pressure dependence of the electrical conductivity.

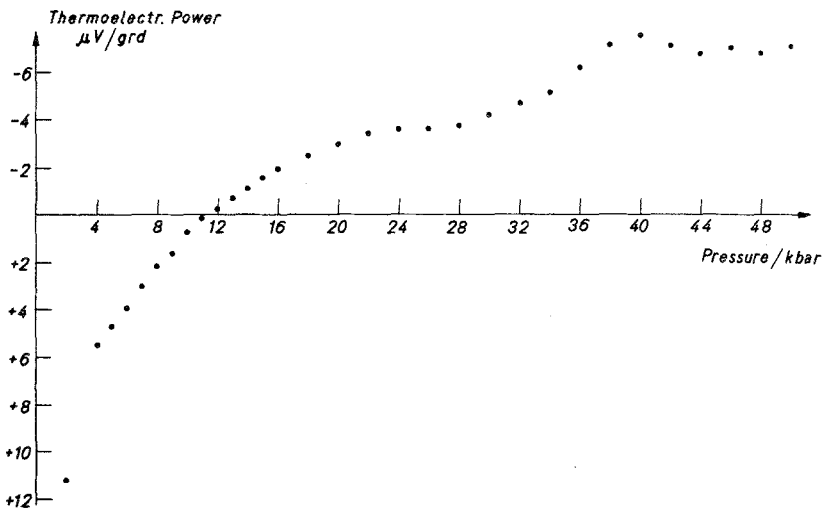


Figure 7
Dependence of the thermoelectrical power from pressure at iron sulphides.

The α -transition is also evident by measuring the thermoelectric power. Figure 7 shows the pressure dependence of this quantity for iron sulphide. It is observed that the thermoelectric power changes its sign around the α -anomaly. This indicates a connection between the crystallographic transition and a strong change of the electrical conduction mechanism. The other $3d$ -transition metal chalcogenides shows only a weak dependence of pressure for the thermoelectric power.

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