

The spectrum of thermally stimulated currents in rock samples from KTB drilling: preliminary results

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Abstract

The technique of thermally stimulated depolarization currents (TSDC) was applied to fine grained amphibolite rock samples extracted from KTB drilling. Each sample was cooled down to liquid nitrogen temperature and consequently heated at a constant rate $b = 4$ K/min while at the same time it was shorted by a sensitive electrometer. Thermocurrent glow curves were detected in the range from 180 to 360 K. By applying the TSDC method, an effort was made to carry out a preliminary analysis of the TSDC spectrum.

Key words *Thermally Stimulated Depolarization Currents (TSDC) – KTB drilling – rocks – relaxation parameters*

1. Introduction

The drilling site of the German Continental Deep Drilling Program (KTB) is located in North-Eastern Bavaria, Germany. The pilot drill hole reached 4000 m and the final depth of the main drill hole is 9101 m. The main lithologies of the KTB borehole are paragneisses and metabasites (Duba *et al.*, 1994). These rock sequences experienced large-scale deformation and metamorphism. The physical properties of KTB rock samples have been reported in a series of papers (Duba *et al.*, 1988; Rauen *et al.*, 1994; Nover *et al.*, 1995).

The present paper presents the preliminary Thermally Stimulated Depolarization Current (TSDC) measurements on an amphibolite sample from KTB drilling. The interest in experimental study springs from the necessity to investigate material systems more complicated than those studied during the few last decades (mainly alkali halides and alkali earth fluorides) (see Varotsos and Alexopoulos, 1985).

Finally, the study of the physical properties of samples from the KTB drilling is expected to contribute to our understanding of large scale geophysical phenomena that take place in the Earth's crust.

2. Theory of the technique

In a number of thermally-stimulated phenomena, the current is measured as a function of temperature following excitation of the sample (see Vanderschueren and Gasiot, 1979). We shall limit this study to conduction due to thermally-released charge carriers while the sample is heat-

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ed under an external voltage following an appropriate excitation at a low temperature. The solid dielectric sample is sandwiched between electrodes in a vacuum cryostat in order to control its heating from a very low temperature in accordance with a predetermined heating program. The contacts applied to the sample are usually evaporated gold or platinum thin films. The sample is placed in series with a dc voltage supply and a sensitive electrometer. The temperature is measured with a thermocouple and the current is recorded as a function of temperature on a computer. Most of the TSDC measurements performed so far have been carried out in this manner.

The general experimental procedure usually involves four steps: 1) the application of a dc bias V_p at a starting temperature T_p ; 2) cooling under this bias to some lower temperature T_0 , usually Liquid Nitrogen Temperature (LNT). Since the relaxation time $t_{(LNT)}$ at LNT is practically infinite, the polarization state attained during the polarizing stage remains frozen, even when switching off the field; 3) changing the bias to another value V_d at T_0 , and 4) heating at a constant rate while maintaining the new bias and recording the current as a function of temperature. If the bias V_d is zero, current peaks are observed during the thermally-activated transition from the polarized state to the equilibrium state. This technique, generally known as the ionic thermocurrent method (ITC) or thermally-stimulated depolarization currents method (TSDC), is widely applied and is used in the present study. If, on the contrary, the bias V_p is zero, current peaks superimposed on the dc conduction current are obtained as a result of the opposite process, *i.e.* thermally-activated transition from the equilibrium state to the polarized state; the currents are generally described by the term thermally-stimulated polarization currents (TSPC). In the general case where both V_p and V_d are not zero, the currents observed are obviously governed by combined polarization and depolarization mechanisms.

A variation of the TSDC method consists of the excitation of a crystalline or amorphous sample by *x*-ray irradiation at room temperature, thus introducing charge carriers to occupy traps. Occupied traps may already exist at that temperature but this technique ensures that all traps

are filled. The sample is subsequently subjected to a dc bias V_p (step 1). This polarization results in an initial «sweeping» of untrapped carriers, driving them to their respective electrodes. When the temperature is increased, detrapping of carriers starts. This is indicated by a weak current ≤ 1 pA. Also, the thermal energy is high enough to assist the spatial redistribution of the existing space charge, thus all free carriers contribute to the conductivity. The conductivity measured during the heating phase of the crystal, in excess of the normal conductivity, is called the thermally-stimulated conductivity. For a single trap depth, information about: a) the magnitude of the trap depth can be obtained from the temperature corresponding to the maximum TSDC; b) the density of traps can be estimated from the area under the TSDC curve, and c) the capture cross-section of the trap can be found from the detailed shape of the TSDC curve. It is the derivation of this information from the experimental data that is of main interest in the interpretation of such TSDC curves. By measuring thermocurrents in the amphibolite rock system and analyzing the resulting curve of $\ln\tau$ against $1/T$ (Arrhenius plot) it is hoped to unravel the possible trapping and conductivity mechanisms existing in the system. This can be done if the parameters of the Arrhenius relation

$$\tau = \tau_0 \exp(E/kT) \quad (2.1)$$

are determined, where τ is the relaxation time of a trapped carrier and E is the «activation energy» of the trap *i.e.* the energy needed for the release of a trapped carrier. In this case τ is equivalent to the reciprocal of the frequency of carrier releases from the trap and is considered to be very large at room temperature. It is characteristic of the kind of traps as well as of the material under investigation.

The polarization time t_p must be considerably greater than τ in order for all traps to be filled. With the field still present, the sample is cooled to a low temperature T_0 at which the available thermal energy is insufficient to release the trapped carriers. Then, the electric field is removed and the sample is heated at a linear rate for convenience of analysis. Here, it should be mentioned that a variety of methods have

been used for the determination of trapping parameters of imperfections in crystals. Among these, the thermally-stimulated depolarization current method (TSDC) offers the advantage of experimental simplicity and potentially yielding much information. It is concluded that this method provides the most reliable determination of trap depth. The results of the theory can be adapted for application to systems involving more than one type of recombination centre.

The thermally-stimulated current method is thus a general method for investigating the electrical properties of high-resistivity solids via the study of thermal relaxation effects and, as such, offers an attractive alternative to the conventional bridge methods or current-voltage-temperature measurements. As far as electronic carriers are concerned, it is closely related to the thermally-stimulated conductivity method (TSC). The mathematics is similar to that found in other non-isothermal techniques such as thermoluminescence and thermally-stimulated electronic emission (Bucci *et al.*, 1966):

$$J(T) = \frac{\Pi_0}{\tau_0} \exp \left[-\frac{E}{kT} - \frac{1}{b\tau_0} \int_{T_0}^T \exp \left(\frac{E}{kT} \right) dT \right] \quad (2.2)$$

where $J(T)$ is the thermocurrent density, Π_0 is the initial polarization of the dielectric, E is the activation energy of the process (identical to the migration enthalpy h_m of the possibly bound migrating defect), b is the constant heating rate, k is Boltzmann's constant, T_0 coincides with LNT and τ_0 is the pre-exponential factor of the usual Arrhenius law, providing the temperature dependence of the relaxation time $t(T)$

$$\ln \tau = \ln \tau_0 + E/kT. \quad (2.3)$$

The space charge peaks are sensitive to the electrode material used and the blocking degree of the sample-electrode interface (Thielen *et al.*, 1996a,b). The polarization state achieved strongly depends on the storage conditions and the prehistory of the sample. Only very rough approximations have been made and several space charge TSDC equations have been derived (Thie-

len *et al.*, 1996a,b). The common point of the different approximations is that the initial rise of the TSDC curve coincides with that of the non-interacting rotating dipoles. An expression for the initial rise can be derived directly from eq. (2.2) by noting that in the region of the initial rise $T = T_0$ and, therefore, the integral in eq. (2.2) is zero. Thus, for the initial rise region we may write

$$I(T) \propto \exp \left(-\frac{E}{kT} \right) \quad (2.4)$$

where $I(T)$ denotes the depolarization current, k the Boltzmann's constant and E the activation energy for the diffusion of free ionic charge carriers, which coincides with the migration enthalpy h_m of the free migrating entities and is a different quantity from the activation energy of the dipolar reorientation. Subsequently, the evaluation of the activation energy E can be attained, whatever model is assumed to describe the depolarization phenomenon.

3. Experimental details

The experiment was conducted in a cryostat which operates from liquid nitrogen temperature up to 380 K. The sample was placed between platinum plated copper electrodes and the temperature was measured by means of a chromel-alumel thermocouple. The depolarization current was measured with a Keithley 617 sensitive electrometer. The polarization field was 5 kV/m and the sample was polarized for approximately 20 min and then rapidly cooled to LNT. The heating rate was kept constant (approximately 4 K/min) during the heating stage of the TSDC run.

The studied material is a fine grained amphibolite extracted from a depth of the order of 4.5 km in the drilling site of the German Continental Deep Drilling program (KTB). The main rock forming minerals of the studied amphibolites are hornblende, plagioclase, garnet together with minor quartz and biotite. Accessories are: Ti-phases (Ilmenite 1-3%), opaques, K-field-spar, apatite and some zircon. The porosity of the sample was less than 1 vol% (Lich *et al.*, 1992; Nover *et al.*, 1995).

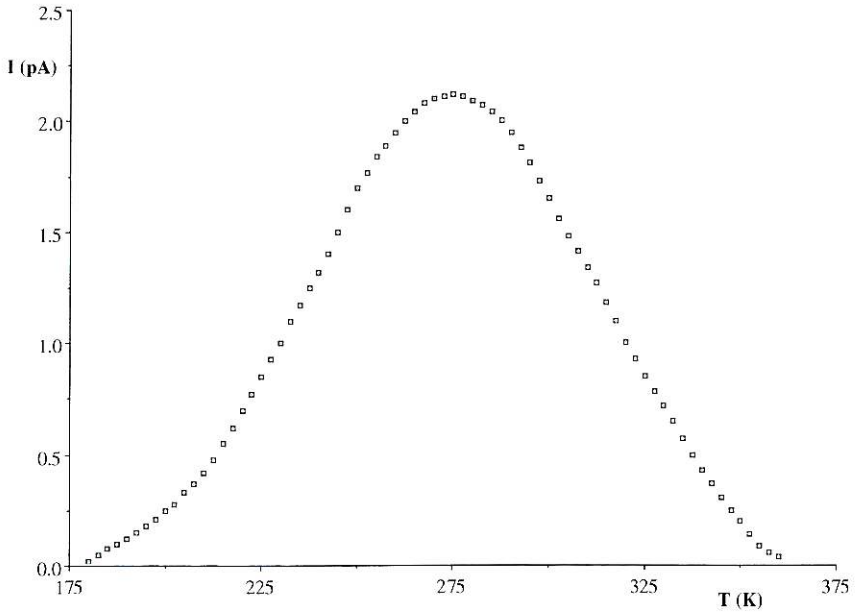


Fig. 1. Thermally stimulated depolarization current spectrum from the amphibolite sample extracted from KTB drilling.

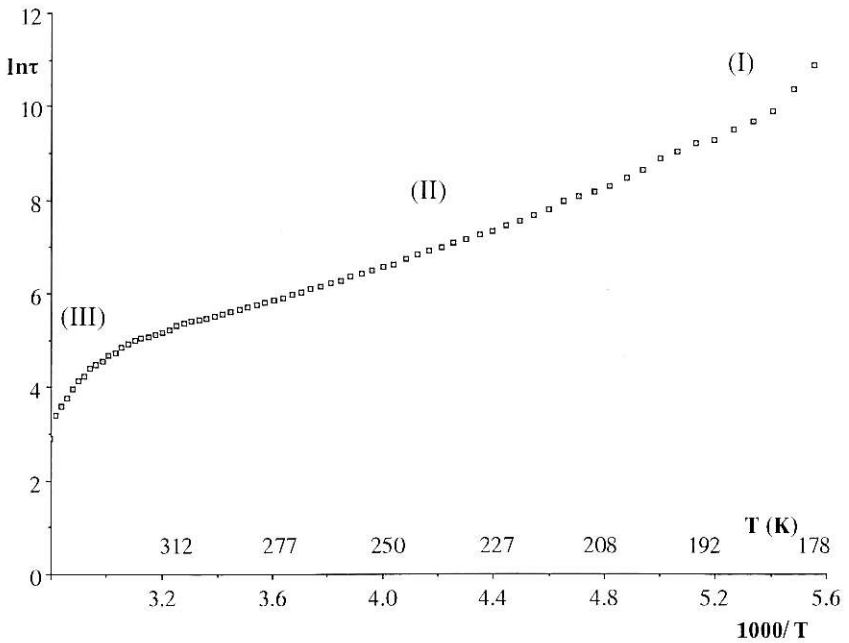


Fig. 2. Variation of relaxation time τ versus $1/T$ for the amphibolite sample.

4. Discussion

The thermal depolarization spectrum of our sample is a broad High Temperature (HT) spectrum with a maximum close to 270 K (fig. 1). We note that the spectrum of amphibolite extracted from such a depth has not been measured before. In order to study the variation in the relaxation time τ with temperature T we applied the TSDC procedure described by Bucci *et al.* (1996).

The resulting τ values are shown in fig. 2 in the form of a plot of $\ln\tau$ against $1/T$. The Arrhenius plot in fig. 2 is not linear, thus indicating the possible coexistence of more than one relaxation mechanisms, or alternatively, a single mechanism with statistically distributed relaxation times. The coexistence of more than one mechanism became evident after applying the TSDC band asymmetry criterion (Triantis *et al.*, 1989). A preliminary analysis can discriminate three main Linear Parts (LP) and the existence of a continuous transition from them. The linear parts LP1, LP2 and LP3 extend to the ranges of: a) low temperatures up to 200 K (with $E = 0.3$ eV); b) from 220 K to 320 K (with $E = 0.2$ eV), and c) at High Temperatures (HT) with $E = 1$ eV respectively.

Recent remarks (Papathanasiou, 1999) favour the space charge origin of the TSDC spectra at temperatures greater than RT. Furthermore the observation of a single peak may be a result of the fact that the contribution of any other mechanisms (e.g., dipolar) may be very small and it is masked by the space charge polarization.

Finally, we note that the present results must be viewed as preliminary. A series of experiments, in order to test the degree of dependence of the TSDC spectrum on the polarization conditions and the electrode material are in progress.

5. Conclusions

Rock samples were investigated by using the TSDC technique. Typical TSDC glow curves were obtained with peaks in the range between

180 and 360 K. The TSDC spectrum was analyzed into monoenergetic bands. After a good computer fitting, three bands were investigated with maximum peaks at 238 K, 270 K and 308 K and activation energy values 0.22, 0.23 and 0.28 eV respectively.

REFERENCES

- BUCCI, C., R. FIESCHI and G. GUIDI (1996): Ionic thermocurrents in dielectrics, *Phys. Rev.*, **148** (2), 816-823.
- DUBA, A., E. HUENGES, G. NOVER and G. WILL (1988): Impedance of black shale from Munsterland borehole: an anomalously conductor? *Geophys. J.*, **94**, 413-419.
- DUBA, A., S. HEIKAMP, W. MEURER, G. NOVER and G. WILL (1994): Evidence from borehole samples for the role of accessory minerals in lower crustal conductivity, *Nature*, **367**, 59-61.
- LICH, S., J. DUYSER, G. GODIZART, S. KEYSSNER and H. DE WALL (1992): *German Continental Deep Drilling Program (KTB) - Geological Survey of Hauptbohrung 0-6000 m*. KTB Report 92-2, R1-R42 rd R. Emmermann (Schweizerbart'sche Verlagsbuchhandlung, Stuttgart).
- NOVER, G., S. HEIKAMP, A. KONTNY and A. DUBA (1995): The effect of pressure on the electrical conductivity of KTB rocks, *Surv. Geophys.*, **16**, 63-81.
- PAPATHANASIOU, A. (1999): Thermal depolarization studies in leukolite (polycrystalline magnesite), *J. Phys. Chem. Solids*, **60**, 407-414.
- RAUEN, A., J. DUYSER, S. HEIKAMP, A. KONTNY, G. NOVER and T. ROCKEL (1994): Electrical conductivity of a KTB core from 7000 m - effect of cracks and ore minerals, *Sci. Drilling*, **4**, 197-206.
- THIELEN, A., J. NIEZETTE, G. FEYDER and J. VANDERSCHUEREN (1996a): Thermally stimulated current study of space charge formation and contact effects in metal-polyethylene terephthalate film-metal system. I. Generalities and theoretical model, *J. Phys. Chem. Solids*, **11**, 1567-1580.
- THIELEN, A., J. NIEZETTE, G. FEYDER and J. VANDERSCHUEREN (1996b): Thermally stimulated current study of space charge formation and contact effects in metal-polyethylene terephthalate film-metal system. II. Influence of polarization conditions, *J. Phys. Chem. Solids*, **11**, 1581-1591.
- TRIANANTIS, D., C. ANASTASIADIS and A. MARKOU (1989): Comments on the asymmetry of the Ionic Thermocurrent Band, *J. Electrostatics*, **22**, 273-277.
- VANDERSCHUEREN, J. and J. GASLOT (1979): Field induced thermally stimulated currents, in *Thermally Stimulated Relaxation in Solids* (Springer-Verlag, Berlin), 135-219.
- VAROTSOS, P. and K. ALEXOPOULOS (1985): *Thermodynamics of Point Defects and their Relation with Bulk Properties* (North Holland, Amsterdam), 132-422.