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# Pressure variation of the electrical conductivity of dolomite $[CaMg(CO_3)_2]$

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The conductivity of dolomite is a decreasing function of pressure, indicating that the dominant mechanism is ionic in alkaline earth carbonates. The activation volume $v^{\mathrm{act}}$ at room temperature is obtained. The curvature observed in the logarithm of the conductivity versus pressure plot is discussed in terms of the activation of multiple mechanisms upon pressure or to the pressure dependence of $v^{\mathrm{act}}$. The estimation of the migration volume $v^m$ from ionic thermocurrent results through the $cB\Omega$ point defect parameter model yields to the evaluation of the association volume $v^{\alpha}$. [S0163-1829(96)07023-3]

## I. INTRODUCTION

Calcite ($CaCO_3$), magnesite ($MgCO_3$), and dolomite [$CaMg(CO_3)_2$ or $CaCO_3$:$MgCO_3$] are typical representatives of the alkaline earth carbonate salts and share rhombohedral crystal structure.[1–3] Dielectric and electric studies in the above so-called ‘‘calcite family’’ can relate the properties of the mixed crystal dolomite [$CaMg(CO_3)_2$] to those of the constituents ($CaCO_3$ and $MgCO_3$). Additionally, we may have a deeper insight into the ionic relaxation and transport properties of ionic crystal structures more complicated than those studied up to date (i.e., alkali halide crystals).[4] Furthermore, due to the fact that part of the Earth's crust consists of carbonate salt rocks, the experimental studies may give valuable information about the geophysical electrical processes. Finally, as the carbonate salts are widespread industrial materials, profit can be gained in order to improve the applications of the aforementioned materials.[5]

The present work is a small piece of our project that is currently developing on the dielectric relaxation and the electrical conductivity measurements on the calcite group materials. We notice that, to the best of our knowledge, only a few works have been reported for single-crystal calcite and (polycrystalline) limestone,[6,7] whereas our very recent results on dolomite and magnesite are in press.[8,9] Here, we report electrical conductivity measurements on dolomite as a function of the hydrostatic pressure. Our target is to characterize the nature of the transport mechanism and, by quantitative analysis of the data, to obtain the value of the activation volume $v^{\mathrm{act}}$.

## II. THEORY

Electrical conductivity measurements versus temperature at ambient pressure lead to the evaluation of the activation energy. A parameter defined from transport experiments under a variety of hydrostatic pressure in crystalline ionic solids is the activation volume $v^{\mathrm{act}}$ defined as the pressure derivative of the activation Gibbs free energy $g^{\mathrm{act}}$ governing the transport process:

$$v^{\mathrm{act}}=\left(\frac{\partial g^{\mathrm{act}}}{\partial P}\right)_T. \tag{1}$$

The activation volume is related to the nature of the migrating species and the volume changes that accompany the defect formation, the lattice distortions during their migration, or the participation in the formation of defect dipolar aggregates. Under certain assumptions,[10–12] the pressure derivative of the ionic conductivity leads to the following equation:

$$v^{\mathrm{act}}=-kT\left[\left(\frac{\partial \ln G}{\partial P}\right)_T-\gamma\kappa_0\right], \tag{2}$$

where $G$ denotes the conductance of the specimen, $\gamma$ the Grüneisen constant and $\kappa_0$ the isothermal compressibility of the material. In the vast majority of ionic crystals, the term $\gamma\kappa_0$ is negligible in relation to the pressure derivative of the conductance, so, we can certainly write

$$v^{\mathrm{act}}\cong-kT\left(\frac{\partial \ln G}{\partial P}\right)_T. \tag{3}$$

Subsequently, at any pressure, the slope of the $\ln G(P)$ diagram directly leads to the value of $v^{\mathrm{act}}(P)$ at that given pressure value $P$.[13] The compressibility $\kappa^{\mathrm{act}}$ of the activation volume is the relative variation of the activation volume upon pressure:

$$\kappa^{\mathrm{act}}=-\frac{1}{v^{\mathrm{act}}}\left(\frac{\partial v^{\mathrm{act}}}{\partial P}\right)_T. \tag{4}$$

Hereafter, for reasons of simplicity the ambient pressure will be also called zero pressure. The preceding equation gives

$$v^{\mathrm{act}}(P)=v^{\mathrm{act}}(0)\exp\left(\int_0^P-\kappa^{\mathrm{act}}dP\right). \tag{5}$$

For further analysis of the experimental data, we make the usual assumption that $\kappa^{\mathrm{act}}$ holds a constant nonzero value and $|\kappa^{\mathrm{act}}P|\ll 1$; then a second-order polynomial isothermal dependence of $\ln G(P)$ can be derived:[13]

$$\ln\left(\frac{G(P)}{G(0)}\right)=\left(\frac{v^{\mathrm{act}}(0)}{kT}-\kappa_0\gamma\right)P-\left(\frac{\kappa^{\mathrm{act}}v^{\mathrm{act}}(0)}{2kT}\right)P^2, \tag{6}$$

where $\kappa_0$ and $\gamma$ take their zero-pressure values.

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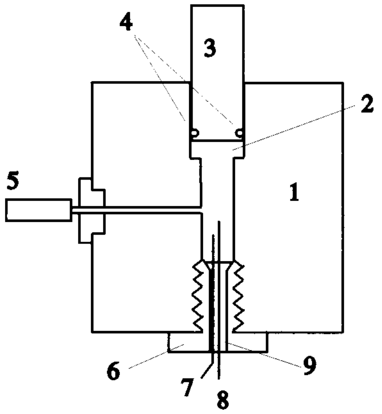

FIG. 1. Simplified vertical cross section of the hydrostatic pressure vessel 1, stainless steel cylinder; 2, pressure chamber, filled with pressure transmitting fluid; 3, stainless steel piston; 4, high pressure O ring; 5, pressure sensor; 6, steel sample holder; 7, thermocouple; 8, central electrode; 9, araldite sealing.

## III. EXPERIMENTAL DETAILS

The conductivity experiments were performed in a pressure vessel constructed by the authors. It is a cylinder-piston apparatus with oil as the pressure transmitting fluid. The pressure cell is shown in Fig. 1. The stainless steel cylinder holds a cylindrical concentric cavity that is filled with the transmitting fluid. The pressure transmitting oil is the Shell Telus 27, appropriate for pressure hydraulic applications. The stainless steel piston exerts an external force to the fluid-filled pressure chamber, resulting in an increase of hydrostatic pressure in the cell. The cylinder was carefully polished to minimize frictional effects and minimize the leakage as well. A high-pressure Teflon-copper O ring, placed on the piston, also prevents the fluid leakage, providing a hermetical sealing. A hole was drilled and a sensitive pressure sensor (Sensotec GM pressure transducer) was rigidly fixed by direct metal-to-metal contact. The sample holder is actually a steel screw. The central steel electrode, as well as the chromel-alumel thermocouple, pass through araldite casting. The araldite sealing provides both excellent hydraulic tightness and sufficient electrical insulation between the central electrode and the pressure cell. The pressure bomb can operate from 1 bar up to at least 3 kbar.

A system of valves can maintain the desired constant value of the uniaxial stress exerted on the piston (and therefore a constant value of the hydrostatic pressure inside the pressure vessel). Additionally, by manual control, we may succeed in any constant rate of the pressure increase or decrease. The indication of a manometer located on the pumping device, by appropriate reduction to the cross section of the piston, gives the hydrostatic pressure value in the pressure vessel. This value agrees, within the experimental errors, with the indication of the digital pressure transducer (which directly probes the pressure inside the pressure cavity). The transducer operates with a precision of about ±3 bars, and its output is connected to a computer via a Keithley DAS 8 PGA A/D card.

The thermocouple is located close to the sample and the reference thermocouple is positioned into an ice bath. The thermoelectric voltage is measured by a 1905a Thurlby digital voltmeter. The connection with the computer is made through a RS232 interface. The communication software we developed permits the continuous and accurate monitoring during the experiment. The vessel is easily kept at room temperature due to the thermal protection of foamy polymer protection and the thermal inertia of the steel vessel itself. The maximum temperature variation throughout the duration of the experiment is less than 2 K. Therefore the pressure vessel is proper for accurate isothermal measurements.[14] The effect of pressure on the thermoelectric voltage of the thermocouple is negligible and does not really improve the precision of the temperature measurement.

The two parallel surfaces of the specimen were painted with silver paste. Afterwards, good quality durable contacts were made by melting a small amount of pure indium and attaching two electrical leads,[15–17] one for each of the sample's surfaces. One of them was fixed to the central electrode and the other to a small cavity drilled onto the upper face of the steel sample holder, which is in direct contact with the steel bomb. For both leads, the rigid fixation was attained by using molten indium.

A Boonton 75c bridge operating from 5 to 500 kHz is employed for the conductance measurements. The leakage conductance (mainly via the araldite insulation) is one or two orders of magnitude smaller than the sample's bulk conductance, in agreement with the published standards.[18] Additionally, the pressure variation of the leakage conductance is within the precision of the bridge and can be considered as practically constant. The error the bridge induces on the determination of the resistance varies from 10% to 15%. The usual way to improve the precision is to take the mean value in a series of successive measurements. Since there might exist some time dependence, we focus on the value as soon as pressure and temperature equilibrium is attained, and afterwards we just detect the time variation, if any exists.

The material we studied is natural polycrystalline greyish, compact rock dolomite from Greece. It is used in industrial applications and was accompanied by the chemical analysis results from Cimprogetti S.P.A. Laboratories, Italy: loss of ignition, 46.91 wt %; $SiO_2$, 0.20 wt %; $Al_2O_3$, 0.12 wt %; $Fe_2O_3$, 0.04 wt %; CaO, 30.51 wt %; MgO, 21.81 wt %. Additional analysis (Institute of Geological and Mining Research, Greece) gave: 0.02 wt % Mn, 0.02 wt % Sr, $<0.01$ wt % K, 0.01 wt % Na, 0.13 wt % humidity.

## IV. RESULTS AND DISCUSSION

The pressure bomb accommodates a two-electrode system and subsequently, ac impedance measurements are proper for the elimination of the space charge contribution.[19] Previous studies on different kinds of rocks have shown that space charge phenomena are present sometimes even at the frequency of 1 kHz.[20] In the present paper, the working frequency is 5 kHz. Our choice was justified, as the conductance values were time independent, for any constant pressure value ranging from 1 to 3000 bars. Although the conductivity from 5 to 500 kHz is frequency dependent, its pressure derivative coincides with that of the pressure derivative of the dc conductivity.[21]

In Fig. 2 we have plotted the logarithm of the conductance *G* versus pressure. The measurements were performed

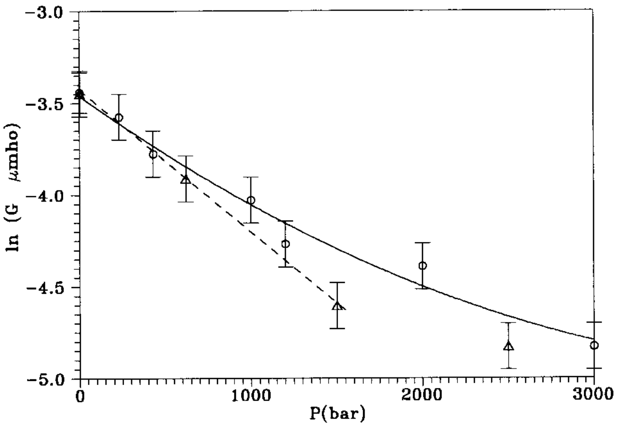

FIG. 2. Pressure dependence of the conductance $G$ of polycrystalline dolomite, at room temperature ($T = 294$ K). The circles correspond to the data obtained on increasing pressure and the triangles to decreasing pressure. The dashed line is fitted to the low-pressure value points, while the curve is a second-order polynomial fit.

at room temperature and at the frequency of 5 kHz. The conductance decreases upon pressure, indicating that the conductivity mechanism is prohibited as pressure is augmenting. The behavior is typical for ionic conduction and can be understood in terms of a nearly hard-sphere model: the increase of pressure brings the ions closer together and, as a result, reduces the mobility of the migrating entities.[22] Consequently, the qualitative result we get from Fig. 2 is that the dominant conductivity mechanism in dolomite, which exhibits ionic characteristics. We also observed that the conductance at a given pressure is, within the experimental errors, approximately independent of the path we followed (i.e., it is the same either on increasing or on decreasing the pressure). Consequently, no dominant hysteresis phenomenon was indicated during a pressurizing cycle.

The curvature in the conductivity plot observed in Fig. 2 is a common feature of some ionic crystals.[14,16,18] The phenomenon shares three explanations:

(i) On increasing the pressure, the electronic conductivity strongly competes with the ionic conductivity mechanism.

(ii) The conductivity plot does not originate from a single conductivity mechanism. The result of adding two exponential curves (each one corresponding to a single mechanism) and then taking the logarithm would give a curved plot. Therefore, the slope of the plot gives the value of an apparent activation volume.

(iii) There exists a single ionic conductivity mechanism described by a pressure-dependent activation volume $v^{\mathrm{act}}(P)$. According to Eq. (4), this is equivalent to a nonzero compressibility $\kappa^{\mathrm{act}}$ of the activation volume. It is difficult to accept the electronic contribution in an ionic insulator, so (i) should not be valid. It is difficult to distinguish which of the two remaining explanations [(ii) or (iii)] is true.

Assuming that different conduction mechanisms take place [assumption (ii)], we fitted the very first experimental points (from 1 to 450 bars) to a straight line. According to Eq. (3) the slope directly gives the activation volume $v^{\mathrm{act}} = 19 \pm 3$ cm$^3$/mole. The advantage of this method is that, whatever the conductivity plot is, we may get the very important atmospheric pressure value $v^{\mathrm{act}}(0)$.

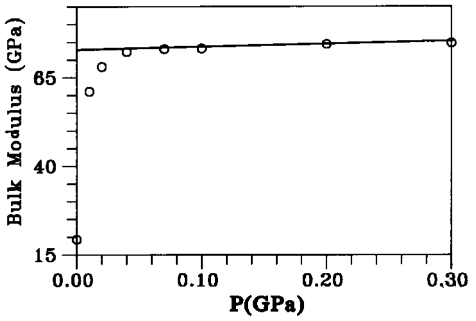

FIG. 3. The bulk modulus of polycrystalline dolomite vs pressure. The circles denote the experimental data estimated from Ref. 23. The solid line is a linear fit of the high-pressure data in order to estimate the bulk modulus of the matrix material at ambient pressure (Ref. 24).

Assuming that the activation volume is pressure dependent [assumption (iii)], we have tried a second-order polynomial fit justified by the physical arguments developed in the theory. By using Eqs. (3) and (4), which have general validity, we get the zero-pressure values $v^{\mathrm{act}} = 16.5$ cm$^3$/mole and $\kappa^{\mathrm{act}} = 2.23$ GPa$^{-1}$. Additionally, $v^{\mathrm{act}}$ varies from 16.5 cm$^3$/mole at $P = 0$ to 11.3 cm$^3$/mole at $P = 3$ kbar. Although the experimental points from a wide pressure range (1 bar to 3 kbars) contribute to the fitting procedure, it is interesting to note that the atmospheric pressure activation volume value $v^{\mathrm{act}}(0)$ is, within the experimental errors, the same as the value extracted from the linear fit [assumption (ii)]. This fact indicates that the value $v^{\mathrm{act}}(0)$ is well defined from our analyses.

Before proceeding to the comparison of the quantities $-(\partial \ln G/\partial P)_T$, $\kappa_0 \gamma$, and $\kappa$, it is very important to review briefly the variation of the elastic properties of a polycrystalline material. In Fig. 3 we display the room-temperature values of the isothermal bulk modulus $B \equiv 1/\kappa$ of polycrystalline dolomite, approximated by the data reported in Ref. 23. The specimen consists of the matrix material (i.e., grains of dolomite) and the porosity. At ambient pressure, the value of the bulk modulus contains a contribution from the matrix compressibility $\kappa_0$ and also from the compressibility due to the porosity. As pressure increases, a rapid increase of the bulk modulus is detected, which originates from the closure of the porosity. At high pressures, $B$ varies almost linearly upon $P$, in the usual manner that most ionic materials behave.[13] It has been proposed that the bulk modulus of the matrix $B_0$ at ambient pressure has to be estimated by linear extrapolation of the high-pressure data to zero pressure.[24] As a conclusion, there exist two different values of the bulk modulus at ambient pressure: one for the material (matrix + porosity), labeled $B \equiv 1/\kappa$, and another one, labeled $B_0 \equiv 1/\kappa_0$, for the matrix itself. $B$ and $B_0$ can be extracted from Fig. 3 in the simple way mentioned above. From Fig. 3, we estimated the quantities $B \cong 19.2$ GPa, $B_0 \cong 72.5$ GPa, and $dB_0/dP \cong 7.5$.

It is necessary to examine whether Eq. (3), obtained by omitting the term $\gamma\kappa_0$ from Eq. (2), is an adequate approximation. Using the value $\gamma \cong 1.7$, which is typical for ionic solids, and the compressibility value $\kappa_0$ for the matrix dolomite, we get $\gamma\kappa_0 = 0.0235$ GPa$^{-1}$ which is 2 orders of magnitude smaller than the term $-(\partial \ln G/\partial P)_T = 7.755$ GPa$^{-1}$. It is obvious that the term $\gamma\kappa_0$ provides a negligible correction to $v^{\mathrm{act}}$, in relation to the precision of the evaluation procedure of the activation volume. Additionally, the compressibility of the polycrystalline dolomite (matrix + porosity) $\kappa = 0.052$ GPa$^{-1}$ is considerably smaller than the term $-(\partial \ln G/\partial P)_T = 7.755$ GPa$^{-1}$, therefore the activation volume we have estimated is indeed a quantity related to the variation of the electrical properties of the material upon pressure, and not the result of the variation of the specimen's dimensions.

The room-temperature conductivity of an ionic insulator usually coincides with the extrinsic associated region conductivity.[24,25] The activation volume can be written as[24]

$$v^{\mathrm{act}} = \frac{1}{2} v^{\alpha} + v^{m}, \tag{7}$$

where $v^{m} \equiv (\partial g^{m}/\partial P)_T$ is the migration volume for the migration process of free (dissociated) charge carriers that contribute to the dc conductivity and $v^{\alpha}$ is the association volume related to the formation (association) of defect dipoles in the lattice. In a simplified manner, the migration volume is the total crystal volume change when the migrating ion moves from its equilibrium position to the saddle point. The association volume is the total crystal volume change when a vacancy initially located at a distant position moves to the immediate vicinity of an heterovalent impurity forming a defect dipole. The migration volume is usually evaluated by performing the conductivity experiments at high temperature. Unfortunately, it is well known that the increase of temperature results in the chemical decomposition (decarbonation) of the carbonate salts.[27,28] At this point, we notice that the decarbonation of dolomite has previously been studied by means of conductivity under pressure[29] above 200 °C. An alternative estimate of $v^{m}$ can be obtained with the assistance of the so-called $cB\Omega$ model[13] that successfully interconnects the point-defect parameters with the bulk properties, through the following relation:

$$v^{m} = B_0^{-1}\left[\left(\frac{dB_0}{dP}\right)_T - 1\right] h^{m}, \tag{8}$$

where $h^{m}$ is the migration enthalpy of the free migrating carriers. Possible candidates can be the vacancies or the small ionic radius impurities such as Na$^{+}$ and K$^{+}$. The same species that contribute to the dc conductivity give rise to the space-charge polarization detected by the most powerful dielectric relaxation technique that is well known as the ionic thermocurrent (ITC) technique,[19] which consists of recording the depolarization current that is emitted by a previously polarized dielectric, as its temperature is raised from liquid-nitrogen temperature up to room temperature. Each relaxation mechanism exhibits a glow-curve-like peak and the analysis can yield to the evaluation of the corresponding migration enthalpy $h^{m}$. In the present case, the fact that the ITC method operates at temperatures lower than the ambient temperature prevents the chemical decomposition of dolomite. Our extensive experimental results[9] showed that the value of $h^{m}$ is distributed from 0.48 to 0.80 eV. Thus, from Eq. (8) we get $v^{m} \cong 4$–$7$ cm$^3$/mole and by returning to Eq. (7) we get $v^{\alpha} \cong 30$–$36$ cm$^3$/mole. These positive values can be considered as the lattice expansion due to the distortion around the defect dipoles.[26,30]

The ratio $\kappa^{\mathrm{act}}/\kappa_0$, where $\kappa_0$ is the matrix compressibility should at most be equal to 5 (Ref. 13) and can serve as a quality factor of the analysis employed. The ratio $\kappa^{\mathrm{act}}/\kappa_0$, where $\kappa_0$ is the compressibility of the matrix dolomite, is equal to 162. This value is about 2 orders of magnitude larger than the theory prediction,[13] but comparable to the large experimental values reported for some ionic crystals such as erbium-doped SrF$_2$ (Ref. 31) and sodium-doped CaF$_2$ (Ref. 32).

## V. CONCLUSION

The decrease of the conductivity upon pressure proves that the dominant transport mechanism in dolomite is ionic. The usual linear fit analysis provides the value of the activation volume $v^{\mathrm{act}} = 19 \pm 3$ cm$^3$/mole. The curvature in the conductivity plots is interpreted either as the activation of additional conductivity mechanisms or as the pressure variation of the activation volume $v^{\mathrm{act}}(P)$, which is estimated by a second-order polynomial fit. The latter assumption gives the zero-pressure values $v^{\mathrm{act}} = 16.5$ cm$^3$/mole and $\kappa^{\mathrm{act}} = 2.23$ GPa$^{-1}$. The combination with dielectric relaxation results and elastic data has led us to the estimation of the association volume $v^{\alpha}$.

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