

Evaluation of the activation volume from ionic conductivity measurements under pressure in porous materials

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A porous (or polycrystalline) dielectric solid is treated as a two-phase heterogeneous system, consisting of an electrolytic conductive matrix and insulating inclusions. The conductivity is described by the Bruggeman's approximation. We derive analytical expressions for the first- and second-order pressure derivative of the conductance. The correction terms to the activation volume value and its compressibility are viewed as functions of the elastic properties of the porous material. The present model is used to interpret experimental results published recently for polycrystalline insulators and compare with a model which has appeared previously. [S0163-1829(98)04647-5]

INTRODUCTION

Significant experimental work on the influence of hydrostatic pressure on the transport properties of insulators has been carried out during recent decades. The interest was mainly focused on the electrical (and dielectric) properties of different types of ionic crystals.¹⁻²² The potential experimental work was accompanied by models, which actually established the theoretical background for the interpretation of the results and the investigation of the formation, migration, and activation processes. During the past decade, the research was directed toward the investigation of polymers.²³⁻²⁹ However, nature provides porous and polycrystalline materials; naturally developed single crystals are rarely found in dimensions large enough to perform electrical measurements. On the other hand, modern technology mainly produces porous materials. It is often impossible to prepare large single crystals (with structure more complex than that of the simple ionic crystals) in controlled conditions and we have to prepare pressurized pellets.⁸

In a recently published paper,³⁰ we proposed a model for evaluating the effect of the porosity modification upon pressure, on the evaluation of the activation volume from conductivity experiments under hydrostatic pressure. We estimated the volume change of the conductive solid frame of a porous material, as pressure increases, in terms of its elastic properties. The aforementioned model is labeled the solid frame modification (SFM) approach. In the present work, the system is approximated by a dielectric matrix, which accommodates insulating spheroid inclusions. Both models are comparatively employed so as to investigate the reliability for the activation volume evaluation from pressure experiments on polycrystalline aggregates.^{21,22}

I. CONDUCTIVITY OF INSULATING DISPERSIONS IN CONDUCTIVE MATRIX

Consider an electrolytic conductive matrix of conductivity σ_m , which accommodates spherical insulating inclusions of conductivity $\sigma_p \rightarrow 0$. Bruggeman has long ago proposed an approximate expression for the effective conductivity σ of a dilute heterogeneous system, in relation to the volume fraction Φ of dispersed phase,³¹

$$\frac{\sigma}{\sigma_m} = (1 - \Phi)^{3/2}. \quad (1)$$

The validity of Bruggeman's approximation was experimentally verified, for a broad range of particle sizes, by de la Rue and Tobias.³² Hanai showed that Eq. (1) holds even for concentrated disperse systems of spherical particles.³³

Labeling G and G_m the conductance of the mixture and the matrix material, respectively, Eq. (1) is modified to

$$\frac{G}{G_m} = (1 - \Phi)^{3/2}. \quad (2)$$

We now consider the case of a polycrystalline (or porous) material consisting of the matrix grains and empty pore space. The grains are bound together tightly and form a concrete solid framework. The voids are free of any fluid and, subsequently, are treated as pure insulators. The volume fraction Φ represents the porosity, which is defined as

$$\Phi = \frac{V_p}{V}, \quad (3)$$

where V_p and V denote the volume of the pore space and the total volume of the porous solid, respectively.

Taking the logarithm of Eq. (2) and differentiating with respect to pressure, we get

$$\left(\frac{\partial \ln G(P)}{\partial P} \right)_T - \left(\frac{\partial \ln G_m(P)}{\partial P} \right)_T = \frac{3}{2} \left(\frac{\partial \ln[1 - \Phi(P)]}{\partial P} \right)_T. \quad (4)$$

We have recently shown that the right-hand-side derivative of the latter equation can be expressed through the isothermal compressibilities κ_m and κ of the matrix grains and the polycrystalline system, respectively:³⁰

$$\left(\frac{\partial \ln[1 - \Phi(P)]}{\partial P} \right)_T = \kappa(P) - \kappa_m(P). \quad (5)$$

With use of Eq. (5), Eq. (4) is written as

TABLE I. The zero-pressure first-order pressure derivative of the conductance of polycrystalline magnesite and dolomite, together with the correction terms determined by the SFM model and the present one. The Grüneissen parameter is assumed to be constant and equal to 1.7 (Ref. 34).

	$\left(\frac{\partial \ln G(0)}{\partial P}\right)_T$ (GPa) ⁻¹	Correction term	
		$(\gamma - \frac{2}{3})\kappa_m(0) + \frac{2}{3}\kappa(0)$ (GPa) ⁻¹ Ref. 30	$(\gamma - \frac{3}{2})\kappa_m(0) + \frac{3}{2}\kappa(0)$ (GPa) ⁻¹ Present work
Magnesite	-7.98 (<i>T</i> =290 K)	0.021	0.022
	-8.36 (<i>T</i> =300 K)	0.023	0.024
	Ref. 22		
Dolomite	-7.755	0.049	0.081
	Ref. 21		

$$\left(\frac{\partial \ln G(P)}{\partial P}\right)_T - \left(\frac{\partial \ln G_m(P)}{\partial P}\right)_T = \frac{3}{2}[\kappa(P) - \kappa_m(P)]. \quad (6)$$

II. ANALYSES OF CONDUCTANCE PLOTS VERSUS PRESSURE

For ionic conduction mechanisms, the percentage variation of the conductance upon pressure in the vicinity of the room temperature yields the activation volume v^{act} , through the following relation:¹⁷

$$\left(\frac{\partial \ln G_m(P)}{\partial P}\right)_T = -\frac{v^{\text{act}}}{kT} + \gamma\kappa_m(P), \quad (7)$$

where k is Boltzmann's constant and γ denotes the Grüneissen parameter, which is usually regarded as pressure independent. Thus, Eq. (6) is modified to

$$\left(\frac{\partial \ln G(P)}{\partial P}\right)_T = -\frac{v^{\text{act}}}{kT} + (\gamma - \frac{3}{2})\kappa_m(P) + \frac{3}{2}\kappa(P). \quad (8)$$

There is no physical argument asserting that the activation volume v^{act} holds a constant value. For isothermal experiments, *we should maintain* the notation $v^{\text{act}}(P)$ for the acti-

vation volume. The percentage of variation of the activation volume is defined through the compressibility κ^{act} of the activation volume:³⁴

$$\kappa^{\text{act}} = -\frac{1}{v^{\text{act}}}\left(\frac{\partial v^{\text{act}}}{\partial P}\right)_T. \quad (9)$$

Taking the pressure derivative of Eq. (8), we get

$$\begin{aligned} \left(\frac{\partial^2 \ln G(P)}{\partial P^2}\right)_T &= \frac{v^{\text{act}}(P)\kappa^{\text{act}}}{kT} + (\gamma - \frac{3}{2})\left(\frac{\partial \kappa_m(P)}{\partial P}\right)_T \\ &+ \frac{3}{2}\left(\frac{\partial \kappa(P)}{\partial P}\right)_T. \end{aligned} \quad (10)$$

It is worthwhile to compare Eqs. (8) and (10) with the equations which were derived within the frame of the SFM approach:³⁰

$$\left(\frac{\partial \ln G(P)}{\partial P}\right)_T = -\frac{v^{\text{act}}}{kT} + (\gamma - \frac{2}{3})\kappa_m(P) + \frac{2}{3}\kappa(P), \quad (11)$$

$$\begin{aligned} \left(\frac{\partial^2 \ln G(P)}{\partial P^2}\right)_T &= \frac{v^{\text{act}}(P)\kappa^{\text{act}}}{kT} + (\gamma - \frac{2}{3})\left(\frac{\partial \kappa_m(P)}{\partial P}\right)_T \\ &+ \frac{2}{3}\left(\frac{\partial \kappa(P)}{\partial P}\right)_T. \end{aligned} \quad (12)$$

TABLE II. Comparative presentation of the zero-pressure second-order pressure derivative of the conductance of polycrystalline magnesite and dolomite and the correction terms implied by the SFM model and the present one.

	$\left(\frac{\partial^2 \ln G(0)}{\partial P^2}\right)_T$ (GPa) ⁻²	Correction term	
		$(\gamma - \frac{2}{3})\left(\frac{\partial \kappa_m(0)}{\partial P}\right)_T + \frac{2}{3}\left(\frac{\partial \kappa(0)}{\partial P}\right)_T$ (GPa) ⁻² Ref. 30	$(\gamma - \frac{3}{2})\left(\frac{\partial \kappa_m(0)}{\partial P}\right)_T + \frac{3}{2}\left(\frac{\partial \kappa(0)}{\partial P}\right)_T$ (GPa) ⁻² Present work
Magnesite	26.81 (<i>T</i> =290 K)	-0.012	-0.025
	40.82 (<i>T</i> =300 K)	-0.012	-0.025
	Ref. 22		
Dolomite	14.88	-2.36	-5.31
	Ref. 21		

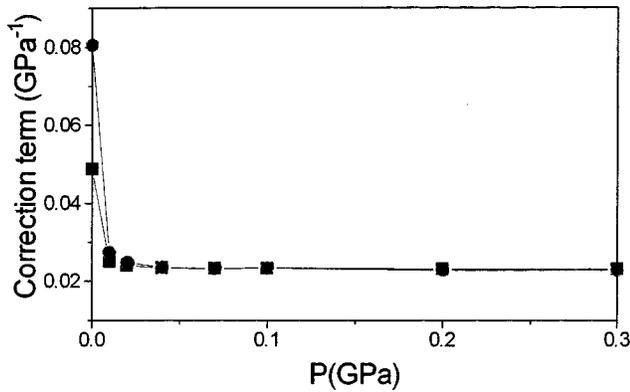


FIG. 1. The correction term for the first-order pressure derivative of the conductance plots of polycrystalline dolomite, as a function of pressure. The squares and the circles correspond to the SFM model and the present one, respectively.

Recently, we have studied the influence of hydrostatic pressure on the conductance of polycrystalline magnesite (MgCO_3) (Ref. 22) and polycrystalline dolomite [$\text{CaMg}(\text{CO}_3)_2$].²¹ The effect of the porosity modification on the evaluation of the activation volume for the aforementioned materials has been discussed elsewhere in terms of the SFM model,^{22,30} which is substantially different from the present one. In Table I, we depict the zero-pressure derivative of the logarithm of the conductance, together with the correction proposed by the two models. Concerning the first-order pressure derivative of the conductance $[\partial \ln G(0)/\partial P]_T$, we note that the corrections implied by both models (SFM and the present one) are close together. The correction does not exceed about 1%, and it is about one order of magnitude lower than the error in defining the slope of the $\ln G(P)$ plots. In Table II, we show the zero-pressure second-order pressure derivative together with the correction terms. It is evident that the present model suggests a correction that is about twice that proposed by the SFM model.

In the above-mentioned tables, we presented the correction terms in detail, in the zero-pressure limit. A graphical comparison between the SFM model and the present one is depicted. In Figs. 1 and 2, we show the correction term for the first- and second-order pressure derivatives of the con-

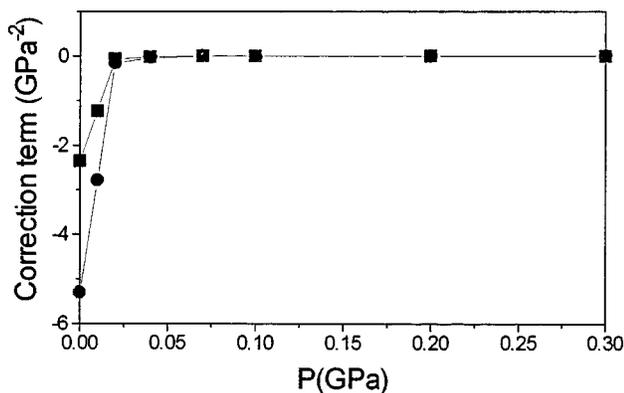


FIG. 2. The correction term for the second-order pressure derivative of the conductance plots of polycrystalline dolomite. The squares and the circles correspond to the SFM model and the present one, respectively.

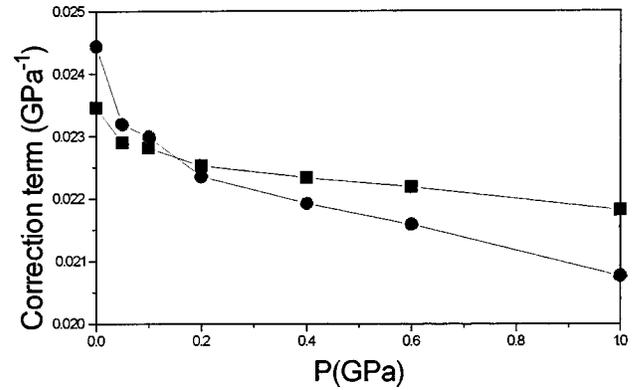


FIG. 3. The correction term for the first-order pressure derivative of the conductance plots for polycrystalline magnesite, as a function of pressure. The squares and the circles correspond to the SFM model and the present one, respectively.

ductance plots, respectively, of polycrystalline dolomite. Figures 3 and 4 correspond to the polycrystalline magnesite.

CONCLUSION

In the present work the porous dielectric solid is represented by a two-phase heterogeneous system, consisting of an electrolytic conductive matrix and insulating inclusions. Starting from Bruggeman's approximation, we derived the correction terms for the first- and second-order pressure derivatives of the conductance plots. The correction determines the accuracy in estimating the activation volume and its compressibility. Working on the experimental results for polycrystalline dolomite and polycrystalline magnesite, we found that the present model is numerically compatible with an older model, called the SFM model. Both approaches provide the background for analyzing the conductance versus pressure experiments on porous or polycrystalline insulators.

ACKNOWLEDGMENTS

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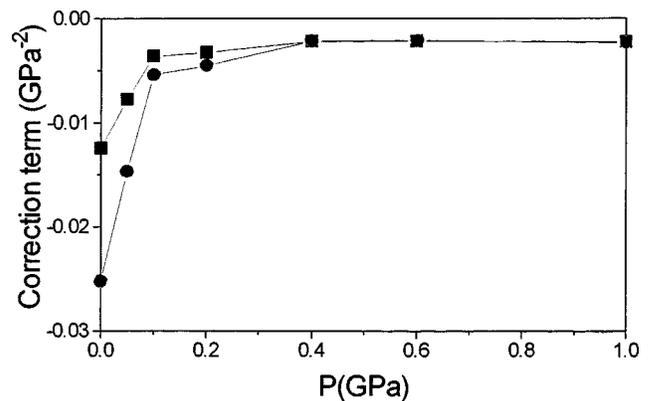


FIG. 4. The correction for the second-order pressure derivative of the conductance plots of polycrystalline magnesite. The squares and the circles correspond to the SFM model and the present one, respectively.

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