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On the case of the negative activation volumes of defects in solids

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ABSTRACT

When conductivity, self-diffusion or electrical relaxation measurements are carried out at various pressures, the results are described in terms of a defect activation volume. Here, we discuss the rare case of negative activation volumes e.g., the one found by Fontanella et al. [Phys. Rev. Lett. 51 (1983) 1992] in the electrical relaxation measurements under pressure in β-PbF$_2$ doped with lanthanum and cerium. This might be of importance for the explanation of electric signals detected before earthquakes, We suggest that this might be due to a small Gruneisen constant γ_i, namely smaller than $\frac{1}{3}$.

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1. Introduction

The major reason for the interest on the fluorite-structured materials during the last three decades, has been the discovery that these systems exhibit superionic conductivity at high temperature. Here we focus on one of them, i.e., β-PbF$_2$, which is probably the most prominent fluoride superionic conductor because of its low transition temperature (≈ 700 K) and high ionic conductivity ($\sigma = 1\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at 800 K; e.g., see Refs. [1,2]). This has been the subject of a large number of investigations. Among these studies, Figueroa et al. [3] have made low temperature dc-conductivity measurements under various pressures on PbF$_2$ either pure or doped with various alkali metals. At their lower temperatures of these measurements at which the conductivity is due to free vacancies thermally dissociated from the electric dipoles consisting of the impurity and the fluorine vacancy (created for reasons of charge compensation), the activation volume v^{act} is given by

$$v^{act} = 1/2 v^a + v^{fm}$$

where v^a, v^{fm} stand for the volumes that correspond to the association process and the free (fluorine) vacancy motion, respectively. Moreover, Figueroa et al. [3] made dielectric

relaxation measurements at various pressures, which give the volume $v^{m,b}$ for the (re)orientation process of the above dipoles. All these volumes determined for all the alkali ions Li$^+$, Na$^+$, K$^+$ and Rb$^+$ have been found to be positive. In addition, Figueroa et al. [3] noticed that the ratio of activation volumes to activation energies (which are, in fact, activation enthalpies designated hereafter with h^{act}), is the same for all dopants. An explanation of this important experimental finding was proposed in Ref. [4], based on model, termed $cB\Omega$ model, that will be summarized later on in Section 2 (cf. Ref. [4]; however, cases of negative activation volumes have not been discussed, see also below). In accordance to this explanation, the ratio v^{act}/h^{act} should *solely* be governed by macroscopic properties of the bulk solid. Actually, it was shown [4] that the migration enthalpy ($h^{f,m}$) and volume ($v^{f,m}$) for the free (f) fluorine vacancy motion, as well as the corresponding quantities $h^{m,i}$, $v^{m,i}$ for the fluorine interstitial (i) migration, which have been determined from conductivity measurements [5,6] under pressure, exhibit ratios $v^{f,m}/h^{f,m}$ and $v^{m,i}/h^{m,i}$ that are not only equal to those v^{act}/h^{act} found by Figueroa et al. [3] but also equal to the value predicted by the $cB\Omega$ model, i.e., the macroscopic properties alone. The same was found [4] to hold for the conductivity measurements in β-PbF$_2$ [7] which lead to values of the ratio v/h for the defect migration as well as for the anion Frenkel defect formation processes.

The main objective of this paper refers to the investigation on whether the $cB\Omega$ model can explain negative values of the defect activation volume. This is interesting for the following reason.

Aspects based on the thermodynamics of point defects [8,9] motivated the study of seismic electric signals (SES), which are low frequency ($\leqslant 1$ Hz) changes of the electric field of the earth that precede [10–19] earthquakes. In particular, these aspects whose basic lines will be summarized later, assume that in the focal area of the impending earthquake—in which the pressure (stress) gradually increases before the final failure—the activation volume for the defect motion may be negative.

The variation of the pressure (P) affects the formation Gibbs energy, g^f, as well as the migration Gibbs energy, g^m, of defects in solids. The defect volumes for the formation process (v^f) and migration process (v^m) are defined as

$$v^f = \frac{dg^f}{dP}\bigg|_T \quad \text{and} \quad v^m = \frac{dg^m}{dP}\bigg|_T \tag{1}$$

where T denotes the temperature. When both processes, i.e., formation (f) and migration (m) are operating, the experimental results are described in terms of an activation Gibbs energy g^{act}, on the basis of which an activation volume is defined:

$$v^{act} = \frac{dg^{act}}{dP}\bigg|_T \tag{2}$$

If experiments refer to migration (m) of a bound (b) defect, e.g., the case of the (re)orientation of electric dipoles consisting of an aliovalent impurity and a neighboring (bound) vacancy [20,21] or interstitial [22,23], the results are described in terms of an activation energy $g^{act,b}$ which is associated with an activation volume $v^{m,b} \equiv (dg^{m,b}/dP)_T$ for the (re)orientation process. In the vast majority of the experiments studying the pressure variation of either the dc ionic conductivity or the diffusion coefficients in various materials v^{act} was found to be positive. The same holds for the $v^{m,b}$ values obtained from electrical relaxation measurements under various pressures. However, some noticeable exceptions have been reported, chief among of which are the following: First, negative v^{act} was found in the case of the dc conductivity measurements by Allen and Lazarus [24] in B4-AgI. Second, negative v^{act} has been also found in water as well as in some polymers (containing water), in which the electrical conductivity—in a certain region—is controlled more by the water than by the polymer [25]. As a third example, we refer to the electrical relaxation measurements at various pressures carried out by Fontanella et al. [26] on β-PbF$_2$ doped with lanthanum and cerium, which showed a single, strong relaxation peak with negative activation volume.

We now briefly describe the aspects that motivated the SES research field [27]. A solid containing electric dipoles due to defects, can emit transient electric signals, termed pressure stimulated currents (PSC), as a result of either increasing or decreasing pressure under isothermal conditions [8,9]. Such electric dipoles are formed due to presence of aliovalent impurities which result in the presence of extra vacancies or interstitials to maintain charge neutrality in the bulk. For example, the addition of divalent cations in an ionic crystal A$^+$B$^-$ produces an equivalent number of cation vacancies [20,21], or trivalent dopants in alkali earth fluorides produce fluorine interstitials [22,23], as mentioned above. A portion of these extra vacancies or interstitials (called bound defects, b) are attracted by the aliovalent impurities and from electric dipoles that can change their orientation in space (the rest of these vacancies or interstitials remain "free", contributing to the dc conductivity of the crystal, as mentioned). The relaxation time $\tau^{m,b}$ for this change of orientation is given by [27]

$$\tau^{m,b} = (\lambda v)^{-1} \exp\left(\frac{g^{m,b}}{k_B T}\right) \tag{3a}$$

or

$$\tau^{m,b} = (\lambda v)^{-1} \exp\left(\frac{s^{m,b}}{k_B}\right) \exp\left(-\frac{h^{m,b}}{k_B T}\right) \tag{3b}$$

where λ denotes the number of jump paths accessible to the jumping species with an attempt frequency v, k_B the usual Boltzmann's constant, and $g^{m,b}$ has been decomposed into an enthalpy $h^{m,b}$ and an entropy $s^{m,b}$ through $g^{m,b} = h^{m,b} - Ts^{m,b}$. The time $\tau^{m,b}$ may decrease or increase upon increasing pressure depending on the sing of the pressure derivative of $g^{m,b}$, which as mentioned above is the migration volume $v^{m,b}$. In other words, the rotation of these electric dipoles becomes slower or faster upon pressurizing if $v^{m,b}$ is positive or negative, respectively. Let us now consider a solid which contains electric dipoles of the aforementioned type which are randomly oriented and have too large $\tau^{m,b}$ value with negative value of $v^{m,b}$. Even if we apply a (small) external electric field, the solid remains practically non-polarized since the electric dipoles retain their random orientation in view of their large $\tau^{m,b}$ value. Let us now assume that we gradually increase the pressure, which reflects a gradual decrease of $\tau^{m,b}$ due to the negative $v^{m,b}$ value. It has been shown [8,9] that a (pressure stimulated) polarization current (PSPC) arises when the pressure reaches a critical value P_{cr} in the neighborhood of which the $\tau^{m,b}$ value becomes (under gradual variation of the pressure versus the time t) sufficiently small so that the dipoles align from a random orientation into the direction of the (external or internal) electric field. The maximum value j_M of the curred density is observed when [9]

$$\frac{d\tau^{m,b}}{dt}\bigg|_{j=j_M} = -1 \tag{4}$$

which results in

$$\frac{bv^{m,b}}{k_B T_M} = -\frac{1}{\tau(P_M)} \tag{5}$$

where b denotes the pressure rate, i.e., $b \equiv (dP/dt)_T$ and $\tau(P_M)$ stands for the relaxation time at the pressure at which j_M is detected. It has been shown [9,28] that the latter two relations hold irrespective if the pressure rate b is constant. In other words, when gradually increasing the pressure in a solid, which is not initially polarized, a transient polarization signal is emitted when the pressure approaches a critical pressure P_{cr} (i.e., when reaching a pressure at which the relation: $bv^{m,b}\tau \approx -k_B T$ is obeyed), which may be smaller than the pressure P_{fr} at which fracture occurs. The important prerequisite for the observation of such a phenomenon is that $v^{m,b}$ should be negative. This is the model suggested [8–10,27] for the observation of a transient electric signal, i.e., SES, *before* an earthquake, in view of the fact that, as mentioned above, the pressure (stress) is gradually increasing in the focal region *before* failure. We clarify that this effect of PSPC may be accompanied by a change of the dielectric constant upon increasing the pressure [29,30].

The above show that the cases in which $v^{m,b}$ is negative, deserve a special attention in view of their practical importance. Here, we make an attempt towards understanding the conditions under which such cases appear. In order to obtain these conditions, we make use of the $cB\Omega$ model [4,31–37] which is summarized in the next section and interconnects g^{act} with bulk properties. In Section 3, we obtain the conditions under which v^m becomes negative and then compare them with the prediction of the dynamical theory for the migration of defects in solids.