Extreme negative mechanical phenomena in the zinc and cadmium anhydrous metal oxalates and lead oxalate dihydrate

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Abstract. The crystal structures and elastic properties of the anhydrous zinc and cadmium oxalates and lead oxalate dihydrate are determined using rigorous first-principles solid-state methods. The three materials are shown to display negative Poisson's ratios (NPR) and to exhibit the negative linear compressibility (NLC) phenomenon. Anhydrous zinc and cadmium oxalates display NLC for a very wide range of external pressures applied in the direction of minimum compressibility in the ranges -1.3 to 5.5 GPa and -1.2 to 2.7 GPa, respectively. The increase of volume in both materials is substantial for pressures larger than 3.6 and 1.8 GPa and the compressibilities become -70.1 and -67.0 TPa⁻¹ for pressures of 5.2 and 2.6 GPa, respectively. The increase of volume is so drastic that these materials become unstable for pressures larger than 5.5 and 2.7 GPa. Lead oxalate dihydrate also displays NLC along the direction of minimum Poisson's ratio for negative pressures in the range -0.05 to -0.08 GPa and undergoes a pressure induced phase transition for relatively low external pressures of the order of 0.1 GPa. The presence of NPR and NLC phenomena in these three materials together with the previous finding of these phenomena for silver oxalate, strongly suggest that other metal oxalate materials could also exhibit an extremely anomalous mechanical behavior.

Introduction

In recent works [1–7], the elastic behavior of small organic acids and metal-organic materials in the solid-state was studied using rigorous first-principles solid-state methods based in Density Functional Theory (DFT) using plane wave basis sets and pseudopotentials to describe the internal electrons [8]. Accurate descriptions of the elastic properties of these materials were obtained by means of extended computational treatments. It was shown that these materials display negative values of the Poisson's ratio (NPR) [9–14] and exhibit the important negative linear compressibility (NLC) phenomenon [15–20]. In particular, anhydrous silver oxalate, was revealed be strongly *auxetic* [21–22] and to exhibit the most extreme form of the negative linear compressibility phenomenon found up to date [7]. For this reason, the study of the elastic properties of silver oxalate was extended to other metal oxalates as the zinc and cadmium anhydrous oxalates, ZnC_2O_4 and CdC_2O_4 , and

lead oxalate dihydrate, $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, with the purpose of analyzing the possible presence of extreme negative mechanical phenomena in other materials of the same chemical group. As it will be shown, the results reported in the present study confirm this hypothesis.

The anhydrous metal oxalates [23] are especially relevant in material science because these materials have important applications in nanomaterials technologies [24–41]. The controlled thermal decomposition process of metal oxalates [29–41] produces nanoparticles of metallic or metal oxide compounds which may be incorporated into a large series of technological and commercial products. Important examples are their use in the production of coatings, pigments, absorbing and shielding materials, nanofibers, electrodes, inkjet thin films, first aid bandages plastics, soaps, skin care products and textiles [24–31] acquiring desirable material properties. In order to obtain antimicrobial effects, metallic ions, as zinc and silver, are incorporated at the stage of synthesis to dental composites and artificial bone materials [42]. Outstanding corrosion protection properties are attained by means of the deposition of zinc oxalate coatings [43]. Anhydrous cadmium oxalate is also employed for obtaining ferrite compounds [44], magnetic materials [45], and complex salts in sol-gel reactions [46–50] and is employed as dopant for obtaining mixed oxide systems [51]. Anhydrous metal oxalates are also useful in thick-film applications [52, 31], as anode materials for lithium-ion batteries [53–56] and as dopants for improving the functionality of conducting polymers and nanomaterials [57]. Because the decomposition of some metal oxalate materials may also be activated mechanically [58–60], it is remarkable that the elastic properties of these materials have not been hitherto reported and their anomalous mechanical behavior has not been noticed. While the metal oxalate pressure induced decomposition was produced by ball milling [58–60], the fact that single crystals become unstable under pressure should be the underlying physical reason for the mechanical decomposition of the zinc and cadmium oxalates. The main aim of this work is to show that the elastic behavior of the zinc and cadmium anhydrous divalent metal oxalates is, as that of the silver anhydrous monovalent metal oxalate [7], very extreme and, therefore, their elastic properties are potentially useful in a large series of technological applications. Moreover, the elastic behavior of the zinc and cadmium oxalates is shown to be analogous suggesting a common mechanical performance of the group of anhydrous divalent metal oxalate materials having structures based in chains formed by alternate oxalate and metal-oxygen polyhedra fragments. This kind of structure-

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function relationships are very important in materials science. They may be used to understand the origin of the special properties of some compounds and to anticipate their existence in structurally related materials with very different compositions.

NPR and NLC materials have enhanced material properties resulting exclusively from their elastic behavior [1]. These properties make them appropriate for an immense range of applications as in textile [61–65] and automotive industries [66], personnel protection [67], biomedicine [68–69], aerospace and defense [70–73], and in many commercial applications requiring filters, sieves, sensors, packaging and insulation [17, 74–75]. In particular, NLC materials have been utilized to develop ultrasensitive pressure-sensing devices, pressure driven actuators, optical telecommunication cables, artificial muscles, next-generation body armor and in biomedical uses [1, 17–18]. Natural NLC materials are very infrequent [20]. Although synthetic procedures and design approaches have been formulated to obtain materials showing specific elastic properties [1, 19, 76–79], the magnitude of the NLC and the range of external pressures for which these natural and synthetic materials show NLC are frequently too small to be useable in practice. The purpose of this and the previous studies [1–7], is to examine the occurrence of negative mechanical phenomena in organic materials because these effects have been studied only occasionally for this class of compounds, exposing a substantial gap in their research. The relevance of this research derives from the wide range of potential applications of these materials, the great versatility of organic synthesis and the wide variety of organic crystalline structure types which may show these effects.

This paper is organized as follows. In the Methods Section, the first-principles solid-state methodology used in this work is described. The main results are reported in the following Section. The first Subsection provides the calculated crystal structures and their associated X-ray powder patterns. The computed elastic properties are then given and their dependence on the orientation of the applied strain is studied. The presence of the NPR and NLC negative mechanical phenomena in the considered materials is also shown. In the section of Discussion a detailed analysis of the results is given. In this section, the deformation of the crystal structures under pressure at the basis of the NLC effect in these materials is also studied. Finally, in the last section, the conclusions of this work are presented.

Methods

Crystal structure optimization

The crystal structures of the anhydrous zinc and cadmium oxalates and lead oxalate dihydrate were modeled using first-principles solid-state methods based in DFT using plane wave basis sets and pseudopotentials [8]. The energy-density functionals employed in this study were the specialized version of Perdew–Burke–Ernzerhof (PBE)

functional [80] for solid materials, PBEsol [81], for the two anhydrous materials and the PBE functional [80] supplemented with Grimme empirical dispersion correction [82] for the dihydrate. The introduction of dispersion corrections improved substantially the description of the hydrogen bonding structure present in the unit cell of lead oxalate dihydrate. These density functionals are implemented in CASTEP computer program [83] a module of the Materials Studio program suite [84]. The pseudopotentials used for C, O, H, Zn, Cd and Pb atoms were standard norm-conserving pseudopotentials [85] given in CASTEP code. The representative volume elements of the materials considered are the corresponding unit cells. Periodic boundary conditions are applied in the calculations. These boundary conditions are not imposed as constraints in the variational procedures since the electron density of the material is represented in terms of periodic functions with the periodicity of the material considered and, therefore, the boundary conditions are satisfied by construction.

The Broyden–Fletcher–Goldfarb–Shanno (BFGS) technique [8, 86] was employed to optimize the atomic positions and unit cell lattice parameters of these materials. The geometries were optimized using a convergence threshold on atomic forces of 0.01 eV/Å. The calculation parameters, the kinetic energy cutoff (ϵ) and k -mesh [87], utilized in the calculations are given in Table S.1 of the Supplementary Material. It must be emphasized that the selected parameters are larger than those usually used in this kind of studies in order to attain reliable crystal structures, energies and values of the computed elastic properties. From the optimized structures, the X-ray diffraction powder patterns were determined [88] using the REFLEX module included in the Materials Studio suite [84].

Determination of elastic tensors

The stiffness tensor needed to calculate the elastic properties of the materials considered was obtained for the optimized crystal structures from stress-strain relationships employing the finite deformation technique [89]. The first and second derivatives of the bulk modulus with respect to pressure were determined by performing fits of the unit cell volumes and associated pressures to a fourth-order Birch–Murnaghan [90] equation of state (EOS). The unit cell volumes in the neighborhood of the equilibrium structures were calculated by optimizing the crystalline structures under the effect of seventeen different applied isotropic pressures within the range from -1.0 to 11.0 GPa. The fits of the pressure-volume data to the chosen EOS were carried out utilizing the EOSFIT 5.2 computer program [91]. The three-dimensional representations of the elastic properties of the materials considered as a function of the orientation of the applied strain were obtained using the EIAM program [92]. Finally, it should be noticed that the optimized crystal structures under pressure were also determined using the BFGS algorithm.

Table 1. Lattice parameters of ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Parameter	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	Vol. (Å ³)	Dens. (g/cm ³)
Zinc oxalate								
DFT	5.7942	5.1505	5.3487	90.0	113.65	90.0	146.2142	3.484
Exp. [93]	5.831	5.123	5.331	90.0	113.20	90.0	146.3712	3.481
Cadmium oxalate								
DFT	5.8453	5.3340	5.8572	90.0	114.21	90.0	166.5586	3.997
Exp. [94]	5.826	5.252	5.832	90.0	113.86	90.0	163.1976	4.079
Lead oxalate dihydrate								
DFT	9.3558	8.0261	7.8393	90.0	90.0	90.0	588.6576	3.738
Exp. [95]	9.053	8.036	7.834	90.0	90.0	90.0	569.9228	3.861

Fig. 1. X-ray powder diffractograms of the anhydrous zinc and cadmium oxalates and lead oxalate dihydrate determined from the calculated and experimental [93–95] geometries using $\text{CuK}\alpha$ radiation.

Results

Crystal structures

The calculated lattice parameters of the crystal structures of the zinc and cadmium oxalates and lead oxalate dihydrate are given in Table 1, where they are compared with the corresponding experimental data [93–95]. The polymorphic form of CdC_2O_4 studied in this paper is the ordered β form [94, 96]. The X-ray powder diffraction patterns of these materials were determined from the optimized and experimental crystal structures and are plotted in Fig. 1. The computed crystal structures of the zinc and cadmium oxalates and lead oxalate dihydrate are shown in Fig. 2. In this figure the atom labelling convention employed in this work for the atoms in the corresponding structures is also displayed.

Elastic properties

The number of non-vanishing elements of the stiffness tensor for materials having monoclinic (anhydrous zinc and cadmium oxalates) and orthorhombic (lead oxalate dihydrate) space symmetries are 13 and 9, respectively [97]. The calculated stiffness matrices, C_{ij} , for the materials considered are reported in Table 2.

The elastic properties of the polycrystalline forms of the considered materials were determined from the computed stiffness tensor elements utilizing the Voigt [98], Reuss [99] and Hill [100] approaches. As in previous studies [1–2, 6–7, 101–106], the Reuss approximation was selected as the best approach because it afforded the best comparison of the results for the calculated bulk modulus with the single crystal bulk modulus determined from the EOS. The calculated elastic properties are reported in Table 3 and the values of the bulk moduli and their first and second pressure derivatives calculated from the EOS are shown in Table 4.

Fig. 2. Computed crystal structures of ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$: (a) View of a single unit cell of ZnC_2O_4 from [001] crystallographic direction; (b) View of a $2 \times 2 \times 2$ supercell of CdC_2O_4 from [001] direction; (c) View of a $2 \times 2 \times 1$ supercell of $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ from [001] direction; The images (b) and (c) are accompanied by pictures showing isolated cadmium and lead oxalate chains in which the atom labelling convention used is displayed. Color codes: C-grey; O-red; H-white; Zn-purple; Cd-clear brown; Pb-green.

Table 2. Computed elastic constants of ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. All the values are given in GPa.

ij	Zinc oxalate	Cadmium oxalate	Lead oxalate dihydrate
11	59.72	47.60	33.65
22	43.30	45.67	23.92
33	279.86	231.98	54.22
44	24.38	19.13	7.12
55	30.20	22.30	5.11
66	56.43	53.64	21.66
12	23.50	29.77	16.44
13	47.00	41.73	7.30
15	-6.31	-7.78	0.0
23	32.66	31.20	6.12
25	-2.12	-6.28	0.0
35	-22.72	-16.96	0.0
46	0.72	-4.53	0.0

Table 3. Calculated elasticity properties of ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The values of the bulk, shear and Young moduli (B , G and E) are given in GPa.

Property	Zinc oxalate	Cadmium oxalate	Lead oxalate dihydrate
B Bulk modulus	35.87	35.85	17.99
G Shear modulus	26.18	18.84	8.32
E Young modulus	63.17	48.10	21.63
ν Poisson's ratio	0.21	0.28	0.30
D Ductility index	1.37	1.90	2.16
H Hardness index	6.35	2.25	0.20
A^U Anisotropy index	3.63	4.63	2.41

Table 4. Calculated first and second bulk modulus pressure derivatives derived from the EOS for ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The bulk moduli computed from the stiffness tensor elements are given in the last row for comparison.

Property	Zinc oxalate	Cadmium oxalate	Lead oxalate dihydrate
EOS			
B (GPa)	42.56±1.51	38.94±1.06	17.63±3.06
B'	3.35±1.31	7.96±1.10	1.75±0.88
B'' (GPa ⁻¹)	1.03±0.36	-1.24±0.63	5.51±2.74
χ^2	0.010	0.060	0.056
Stiffness tensor			
B (GPa)	35.87±1.31	35.85±0.50	17.99±1.74

Fig. 3. Elastic properties of anhydrous zinc oxalate as a function of the orientation of the applied strain: (a) Compressibility; (b) Young modulus; (c) Maximum shear modulus; (d) Surfaces of minimum (red) and maximum (green) Poisson's ratio. The maximum values of the compressibility, Young modulus, shear modulus and Poisson's ratio are 17.73 TPa⁻¹, 244.01 GPa, 56.44 GPa and 0.62, respectively.

Elastic properties as a function of the orientation of the applied strain

The spatial representations of the elastic properties of the materials under study as a function of the orientation of the applied strain are shown in Fig. 3, Fig. 4 and Fig. 5. They were obtained using the EIAM computer program [92]. For the case of the shear modulus and Poisson's ratio, depending on two directions, the subfigures (c) and (d) provide representations of the surfaces of maximum G and ν . These

surfaces are formed with the maximum values of these properties for a given direction of the longitudinal strain and all possible transverse directions [92]. The surfaces of minimum Poisson's ratio are also given in Figs. 3(d), 4(d) and 5(d). As may be observed, the three considered materials display negative values of the minimum Poisson's ratio. The precise values of the minimum and maximum values of Poisson's ratios together with the associated longitudinal and transverse directions are reported in Table 5.

Fig. 4. Elastic properties of anhydrous cadmium oxalate as a function of the orientation of the applied strain: (a) Compressibility; (b) Young modulus; (c) Maximum shear modulus; (d) Surfaces of minimum (red) and maximum (green) Poisson's ratio. The maximum values of the compressibility, Young modulus, shear modulus and Poisson's ratio are 14.48 TPa^{-1} , 197.26 GPa , 33.85 GPa and 0.79 , respectively.

Fig. 5. Elastic properties of lead oxalate dihydrate as a function of the orientation of the applied strain: (a) Compressibility; (b) Young modulus; (c) Maximum shear modulus; (d) Surfaces of minimum (red) and maximum (green) Poisson's ratio. In this case, the surface of minimum ν is very small. The maximum values of the compressibility, Young modulus, shear modulus and Poisson's ratio are 30.02 TPa^{-1} , 52.23 GPa , 21.66 GPa and 0.67 .

Unit cell volumes and lattice parameters as a function of external applied pressures

In order to study the negative linear compressibility phenomena in ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and to analyze their deformation under pressure, the crystal structures of these materials were optimized under the effect

of different external pressures. The computed unit cell volumes and lattice parameters of anhydrous zinc oxalate for sixteen different external pressures directed along the minimum compressibility direction, $U_{min}^C = (-0.16, 0.0, 0.99)$, are given in Table S.2 of the Supplementary Material. The variation of the volume and parameters as a function of the applied pressure are shown in Fig. 6. Similarly, the computed unit cell volumes and lattice parameters of this material for eighteen different external isotropic pressures are given in Table S.3 of the Supplementary Material and displayed in Fig. 7. For anhydrous cadmium oxalate, the calculated volumes and lattice parameters under the effect of eighteen pressures directed along the direction of minimum compressibility, $U_{min}^C = (-0.31, 0.00, 0.95)$, are reported in Table S.4 of the Supplementary Material and plotted in Fig. 8. The volume and parameters for this material submitted to twelve different isotropic pressures are provided in Table S.5 and displayed in Fig. 9. Finally, for lead oxalate dihydrate, the unit cell volumes and parameters under sixteen different pressures applied in the direction of minimum Poisson's ratio, $U_{min}^L = (0.66, -0.71, -0.25)$, are given in Table S.6 and plotted in Fig. 10. The corresponding results for this material submitted to twenty isotropic pressures are given in Table S.7 and shown in Fig. 11.

Discussion

Crystal structures

As may be observed in Table 1, the results obtained for the lattice parameters of the considered materials are in good agreement with experiment, the differences in the computed unit cell volumes and densities being of the order of 0.2, 2.0 and 3.3% for ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, respectively. The excellent agreement in the calculated X-ray powder patterns of these materials (Fig. 1) provides additional support to the theoretical treatment employed for these materials.

The structure of the unit cell of ZnC_2O_4 , shown in Fig. 2(a), is composed of chains formed with alternate oxalate C_2O_4 and ZnO_4 planar groups. The chains are held together by means of weak van der Waals forces only. Similarly, as shown in Fig. 2(b), the structure of CdC_2O_4 is based in chains composed of alternate oxalate fragments and CdO_6 polyhedra. However, the different chains in cadmium oxalate are bonded through $\text{Cd} - \text{O}$ bonds. Finally, as shown in Fig. 2(c), the structure of lead oxalate dihydrate is formed with folded zig-zag chains of alternate oxalate and PbO_7 polyhedra. The lead atom in this material is coordinated with six oxygen atoms belonging to four different oxalate fragments and one oxygen atom from a water molecule. Therefore, this water molecule is structural, the other one being held to the structure by means of hydrogen bonds only (free water).

Table 5. Minimum and maximum Poisson's ratios for ZnC_2O_4 , CdC_2O_4 and $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The directions for the associated longitudinal and transverse directions are also given.

$\nu_{\min}$	$U_{\min}^L$	$U_{\min}^T$	$\nu_{\max}$	$U_{\max}^L$	$U_{\max}^T$
Zinc oxalate					
-0.29	(0.72, -0.69, 0.00)	(0.69, 0.72, 0.00)	0.62	(0.40, 0.26, -0.88)	(-0.65, 0.60, -0.47)
Cadmium oxalate					
-0.26	(-0.70, -0.71, 0.06)	(0.70, -0.69, 0.09)	0.79	(-0.38, 0.30, 0.87)	(0.62, -0.62, 0.48)
Lead oxalate dihydrate					
-0.07	(0.66, -0.71, -0.25)	(0.62, -0.70, -0.36)	0.67	(1.00, 0.00, 0.00)	(0.00, 1.00, 0.00)

Fig. 6. Calculated unit cell volumes and lattice parameters of ZnC_2O_4 as a function of the applied external pressure directed along the minimum compressibility direction, $U_{\min}^C = (-0.16, 0.0, 0.99)$. **Fig. 7.** Calculated unit cell volumes and lattice parameters of zinc oxalate as a function of the applied isotropic pressures.

Mechanical stability

The fulfilment of the Born mechanical stability conditions [107–108] was analyzed from the calculated stiffness matrices reported in Table 2. The necessary and sufficient condition for mechanical stability is that all eigenvalues of the C matrix be positive [108]. The C matrices were diagonalized numerically and all eigenvalues were found to be positive. Hence, it follows that the crystalline structures of the zinc and cadmium oxalates and lead oxalate dihydrate are mechanically stable.

Elastic properties

The calculated ductility indices (Table 3) for the materials studied were $D = 1.37$, 1.90 and 2.16 , respectively.

Consequently, while zinc oxalate is a brittle material, the cadmium and lead oxalates are ductile [109–110]. The calculated Vickers hardness for the materials considered, $H = 6.35$, 2.25 and 0.20 , respectively. Thus, zinc oxalate is a material of intermediate hardness and the cadmium and lead oxalate materials have low and very low harnesses [111, 106]. The values of the universal anisotropy index [112–113] are $A^U = 3.63$, 4.63 and 2.41 , respectively, and, therefore, the considered materials have a significant elastic anisotropy. The large elastic anisotropy results from the very different values of the stiffness tensor elements, C_{ii} ($i = 1, 2, 3$), along the different directions (see Table 2).

Fig. 8. Calculated unit cell volumes and lattice parameters of CdC_2O_4 as a function of the applied external pressure directed along the minimum compressibility direction, $U_{\min}^C = (-0.31, 0.00, 0.95)$.

Fig. 9. Calculated unit cell volumes and lattice parameters of cadmium oxalate as a function of the applied isotropic pressures

Negative Poisson's ratios

The Poisson's ratio [14] is defined, for a stress applied to a solid material along a certain direction, as the negative value of the ratio of the subsequent differential transverse and longitudinal strains, $\nu = -\delta\epsilon_{\text{trans}}/\delta\epsilon_{\text{long}}$. In this definition, the strain ϵ_i is the variation of the solid size along the direction i divided by the initial size, $\epsilon_i = \Delta L_i/L_i$. In the majority of cases, ν is positive because if a positive pressure is applied along a certain direction, a contraction of the solid along the longitudinal direction and an expansion along all the transverse directions is expected. Nevertheless, in some cases a solid material may behave in a counterintuitive way and anomalous negative Poisson's ratios (NPR) [9–14] can be

found for certain longitudinal and transverse directions. NPR materials laterally expand when they are stretched or laterally shrink when compressed.

Due to the well-known relationship between the value of the elastic anisotropy index and the minimal and maximal values of the Poisson's ratio [92, 114], there were cogent reasons to study the possible anomalous elastic behavior of the considered materials. Thus, the dependence of the elastic properties of these materials with the direction of the applied strain was obtained and analyzed in detail. As may be seen in Table 5 and Fig. 3, Fig. 4 and Fig. 5, the three materials show negative values of the minimum Poisson's ratio. The precise values are -0.29 , -0.26 and -0.06 , respectively.

Fig. 10. Calculated unit cell volume of lead oxalate dihydrate as a function of the applied external pressure directed along the minimum Poisson Ratio direction, $U_{min}^L = (0.66, -0.71, -0.25)$.

Fig. 11. Calculated unit cell volumes and lattice parameters of lead oxalate dihydrate as a function of the applied isotropic pressures.

Negative linear compressibility

The occurrence of negative values of the Poisson's ratio in a given material is often accompanied by the presence of negative linear compressibility phenomenon [1–2, 6–7]. The overall compressibility (the inverse of bulk modulus) measures the relative change of the volume of a material as a response to a pressure variation. It must be positive for space unconstrained solid materials which are thermodynamically and mechanically stable and are submitted to isotropic pressures [14, 115–116]. Hence, a material submitted to a hydrostatic (isotropic) pressure cannot increase its volume, unless it is unstable. The negative linear compressibility (NLC) phenomenon is not related to unstable materials. There are two types of NLC [1–7, 20]: (a) *Anisotropic linear compressibility* (ANLC): Increase of the volume of a material when is submitted to a uniform compression directed along a given direction. In this case the directional derivative of the volume with respect to pressure is negative, i.e., $k^V = -1/V \cdot (\partial V / \partial P_i)_p$, where V stands for the unit cell volume

and P_i is an external pressure applied along a certain direction u_i ; (b) *Isotropic linear compressibility* (INLC): Increase of one or two single dimensions of the unit cell of a material under the application of an isotropic pressure. Now, $k^i = -1/a_i \cdot (\partial a_i / \partial P)_p$, where a_i is a certain parameter of the unit cell, is negative. In this case, the volume does not increase and the positive variation of the parameters in some directions is compensated by a larger negative variation of the parameters in the remaining directions.

The response of a solid material can be completely different when is submitted to isotropic and anisotropic pressures. For example, in previous works, the four possible cases have been observed: *i)* Materials exhibiting INLC and ANLC, as the croconic acid, oxalic acid dihydrate and uranyl squarate monohydrate [1–4,6]; *ii)* Materials exhibiting INLC only, as the silver oxalate [7]; *iii)* Materials displaying ANLC only, as the anhydrous oxalic acid [2]; *iv)* Normal materials which do not show these effects. The ANLC and INLC phenomena in the materials considered are studied in the next Sections.

Table 6. Calculated compressibilities ($k_V = -1/V \cdot (\partial V/\partial P)_P$) of zinc oxalate for applied external pressures directed along U_{min}^C direction between -0.40 GPa and -5.20 GPa.

P (GPa)	$k_V(\text{TPa}^{-1})$	P (GPa)	$k_V(\text{TPa}^{-1})$	P (GPa)	$k_V(\text{TPa}^{-1})$
-0.40	-5.22	1.60	-10.07	3.60	-11.03
-0.20	-6.23	1.80	-10.32	3.80	-12.44
0.00	-6.93	2.00	-10.48	4.00	-14.80
0.20	-7.44	2.20	-10.53	4.20	-18.45
0.40	-7.87	2.40	-10.48	4.40	-23.74
0.60	-8.25	2.60	-10.35	4.60	-31.11
0.80	-8.63	2.80	-10.18	4.80	-40.99
1.00	-9.01	3.00	-10.04	5.00	-53.85
1.20	-9.40	3.20	-10.03	5.20	-70.14
1.40	-9.76	3.40	-10.30	-	-

Table 7. Calculated compressibilities ($k_V = -1/V \cdot (\partial V/\partial P)_P$) of cadmium oxalate for applied external pressures directed along U_{min}^C direction between -0.40 GPa and -2.50 GPa.

P (GPa)	$k_V(\text{TPa}^{-1})$	P (GPa)	$k_V(\text{TPa}^{-1})$	P (GPa)	$k_V(\text{TPa}^{-1})$
-0.40	-14.27	0.60	-15.57	1.60	-18.24
-0.30	-13.51	0.70	-15.99	1.70	-19.33
-0.20	-13.07	0.80	-16.32	1.80	-21.00
-0.10	-12.91	0.90	-16.57	1.90	-23.42
0.00	-12.98	1.00	-16.73	2.00	-26.82
0.10	-13.23	1.10	-16.83	2.10	-31.40
0.20	-13.61	1.20	-16.91	2.20	-37.43
0.30	-14.08	1.30	-17.01	2.30	-45.17
0.40	-14.59	1.40	-17.20	2.40	-54.92
0.50	-15.10	1.50	-17.57	2.50	-66.97

Table 8. Calculated compressibilities ($k_V = -1/V \cdot (\partial V/\partial P)_P$) of lead oxalate dihydrate oxalate for applied external pressures directed along U_{min}^L direction between -0.081 GPa and -0.055 GPa.

P (GPa)	$k_V(\text{TPa}^{-1})$	P (GPa)	$k_V(\text{TPa}^{-1})$
-0.081	35.877	-0.069	-423.099
-0.079	-4.777	-0.067	-363.484
-0.077	-61.065	-0.065	-297.220
-0.075	-134.627	-0.063	-228.465
-0.073	-227.082	-0.061	-160.613
-0.072	-280.891	-0.059	-96.353
-0.071	-340.014	-0.057	-37.737
-0.070	-404.641	-0.055	13.764

NLC in anhydrous zinc oxalate.

The variation of the optimized unit cell volume and lattice parameters of zinc oxalate as a function of the external pressures applied along the direction of minimum compressibility (nearly the of c axis in this case) are displayed in Fig. 6. The unit cell volume increases upon anisotropic compression for pressures ranging from -0.96 to 5.24 GPa. Hence, ZnC_2O_4 exhibits ANLC in this range. Additional theoretical calculations revealed that the compressibility becomes positive in the negative pressure side at -1.25 GPa.

The computed compressibilities of zinc oxalate are shown in Fig. 12 and the corresponding values from -0.40 to 5.20 GPa are reported in Table 6. The magnitude of negative compressibility increases rapidly for a large portion of the pressure range beginning at 3.6 GPa. At $P=3.60$ GPa, the compressibility is $k_V = -11.0 \text{ TPa}^{-1}$ and at $P=5.20$ GPa is $k_V = -70.1 \text{ TPa}^{-1}$. The volume expansion is so large that the material becomes unstable for pressures near 5.50 GPa.

The calculated unit cell volumes and lattice parameters of zinc oxalate as a function of different applied isotropic pressures are plotted in Fig. 7. Under isotropic pressures, zinc oxalate presents an irregular behavior of the lattice parameters for pressures between -1.0 GPa and 0.5 GPa, and the c lattice

parameter oscillates slightly in this range. Zinc oxalate displays INLC intermittently in this range. However, the magnitude of the INLC in zinc oxalate seems to be very small and, in comparison with the ANLC, is not significant since as was shown in the previous Section, this material displays a large ANLC effect for a wide range of applied external pressures directed along the minimum compressibility direction.

The mechanical behavior of zinc oxalate under isotropic pressures is completely different to that for anhydrous silver oxalate since it was shown in a previous work [7] that the later material presents the more extreme INLC effect found up to date.

NLC in anhydrous cadmium oxalate

As can be observed in Fig. 8, the unit cell volume of cadmium oxalate increases upon anisotropic compression for pressures ranging from -1.18 to 2.67 GPa and, consequently, exhibits ANLC in this range. The compressibility becomes positive in the negative pressure side at -1.20 GPa. The computed compressibilities are displayed in Fig. 13 and given in Table 7. The magnitude of negative compressibility increases rapidly from 1.8 GPa. At $P=1.80$ GPa, the compressibility is $k_V = -21.0 \text{ TPa}^{-1}$ and at $P=2.50$ GPa is $k_V = -67.0 \text{ TPa}^{-1}$.

As it occurred for zinc oxalate, the volume expansion becomes so drastic that the material becomes unstable when the external pressures are larger than about 2.70 GPa.

The calculated unit cell volumes and lattice parameters of cadmium oxalate as a function of different applied isotropic pressures are plotted in Fig. 9. Under isotropic pressures, cadmium oxalate does not show any sign of isotropic negative linear compressibility.

Fig. 12. Calculated compressibilities ($k_V = -1/V \cdot (\partial V/\partial P)_P$) of zinc oxalate as a function of the applied external pressure directed along the minimum compressibility direction in the pressure range from -0.4 GPa to 5.2 GPa.

Fig. 13. Calculated compressibilities ($k_V = -1/V \cdot (\partial V/\partial P)_P$) of cadmium oxalate as a function of the applied external pressure directed along the minimum compressibility direction in the pressure range from -0.4 GPa to 2.5 GPa.

Fig. 14. Calculated compressibilities ($k_V = -1/V \cdot (\partial V/\partial P)_P$) of lead oxalate dihydrate as a function of the applied external pressure directed along the minimum Poisson ratio direction in the pressure range from -0.08 GPa to -0.05 GPa.

NLC in lead oxalate dihydrate

As may be noticed in Fig. 10, this material exhibits ANLC for a small pressure range, from -0.055 and -0.078 GPa. The computed compressibilities are shown in Fig. 14 and given in Table 8. The magnitude of the negative compressibility varies rapidly in this pressure range and attains a maximum at $P = -0.069$ GPa, where it becomes $k_V = -423.1$ TPa⁻¹. While the magnitude of the NLC is much larger than for the zinc and cadmium oxalates, the pressure range is much narrower. Although the NLC magnitude is very large, is nearly the half of the value found recently for silver oxalate [7] when this material is submitted to isotropic pressures, -831.9 TPa⁻¹. The magnitude of the ANLC in silver oxalate is the largest found up to date, the ANLC pressure range (from -0.51 to 13.4 GPa) being extremely wide [7].

As shown in Fig. 10, the crystal structure of lead oxalate dihydrate has a very large volume decrease for anisotropic positive pressures directed along the direction of the minimum Poisson ratio larger than +0.08 GPa. This is due to the fact that this material undergoes a pressure induced phase transition. The lattice parameters and atomic positions of the new phase under a pressure value of 0.092 GPa directed along the direction of the minimum Poisson ratio are provided as Supplementary Material in a file of CIF (Crystallographic Information File) type.

Lead oxalate dihydrate also undergoes a phase transition when is submitted to isotropic pressures near 5.85 GPa, as observed very clearly in Fig. 11. The lattice parameters and atomic positions of this pressure induced phase at 6.0 GPa are also reported as Supplementary Material in a file with CIF format.

Crystal structure deformation under anisotropic pressures

To assess the crystal structure variations at the basis of the INLC phenomena in the anhydrous zinc and cadmium oxalates and lead oxalate dihydrate, the optimized structures under pressure were analyzed in detail.

Deformation of the crystal structure of ZnC_2O_4

The main structural variations associated to the volume change in zinc oxalate under the effect of anisotropic pressures can be seen in Table S.8 of the Supplementary Material. In this table, the structural changes between the structures optimized at the pressures -0.286, 0.0, and 0.283 GPa are provided. The lattice parameter b is very similar at the three pressures. The application of positive pressures along U_{min}^c does no change significantly the oxalate fragment geometry but leads to a large decrease of the Zn – O1 distance which is nearly the half of the decrease of the c lattice parameter, that is, the distance between two ZnO_4 groups in the same chain (Zn – Zn** distance, see Fig. 2). The ZnO_4 groups become shorter along c direction and longer along the perpendicular direction. The O2 – Zn – O1 angle increases. The decrease in c lattice parameter is accompanied by the increase of the interchain distance Zn – Zn*** (along a axis). The interchain distance

$\text{Zn} - \text{Zn}^*$ (along b axis) remains nearly constant. Since the increase of the interchain distance is larger than the decrease of the intrachain distances the total volume increases leading to the ANLC in zinc oxalate.

Deformation of the crystal structure of CdC_2O_4

As shown in Table S.9 of the Supplementary Material, the application of pressures along $U_{\min}^c$ does not change significantly the geometry of the oxalate fragments but leads to a large decrease of the $\text{Cd} - \text{O}$ distances which is the main responsible of the decrease of the c lattice parameter. The lattice parameter c is identical to the distance between two CdO_6 groups in the same chain ($\text{Cd} - \text{Cd}^*$ distance, see Fig. 2). This decrease is accompanied by the increase of the interchain distance ($\text{Cd} - \text{Cd}^{\oplus}$). Since the increase of the interchain distance (see a lattice parameter) is larger than the decrease of the intrachain distance, the total volume increases leading to the ANLC in cadmium oxalate. The mechanism is similar to that found in zinc oxalate, but in this case the chains do not interact by means of weak van der Waals forces since they are bonded through $\text{Cd} - \text{O}$ bonds (see Fig. 2(b)). The larger rigidity of the interaction between the chains leads to the emergence of the instability in the structure at a much smaller applied external pressure in cadmium oxalate.

Deformation of the crystal structure of $\text{PbC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

As may be seen in Table S.10 of the Supplementary Material, the application of increasingly large negative (expansive) pressures along $U_{\min}^L$ within the range -0.055 and -0.078 GPa leads to a large decrease of the $\text{Pb} - \text{Pb}^{\#}$ distances within a given folded chain (see Fig. 2(c)). At the same time, the interchain distance along a direction (the $\text{Pb} - \text{Pb}^*$ distance in Table S.10) increases and the interchain distance along b direction decreases (see $\text{Pb} - \text{Pb}^{**}$ distance). The distances along c direction remain almost constant. Since the decrease of the interchain distances along b direction is much larger than the increase of the distance along a direction, the total unit cell volume decreases and, consequently, this material shows ANLC.

Conclusions

The anhydrous zinc and cadmium oxalates and lead oxalate dihydrate were studied using first-principles solid-state methods based in Density Functional Theory employing plane waves and pseudopotentials. The computed crystal structures and X-ray powder diffraction patterns were in very good agreement with their experimental counterparts. The elastic properties of these materials were also determined. Since these properties have not been measured experimentally, they were predicted. A large set of relevant elastic data, including the bulk, Young and shear moduli, the Poisson's ratio, ductility, hardness and anisotropy indices and the bulk modulus pressure derivatives were reported. The materials considered were found to be very anisotropic and to display the important NPR and NLC phenomena.

The elastic behavior of the anhydrous zinc and cadmium oxalates was found to be analogous suggesting a common mechanical performance of the group of anhydrous divalent metal oxalate materials having structures based in chains formed by alternate oxalate and metal oxygen polyhedra. In these systems, the ANLC effect appears to be due to the fact that when an anisotropic compression is made along a direction near to the direction of the chains, although the intrachain distances decrease significantly, the interchain distances along the perpendicular directions increase to a larger extent resulting in a net increase of the unit cell volume. These structural variations are similar to the NLC mechanisms encountered in previous works [1–2] for the croconic and oxalic acids. These materials are formed from structural elements as sheets or chains linked through weak van der Waals interactions. In these materials, the weak bonding between the sheets or chains also accommodates the structural variations arising from the application of pressure but the resulting deformations are anomalous and negative values of the compressibility are obtained due to the large increase of the intersheet or interchain distances. For uranyl squarate monohydrate [6] and silver oxalate [7], the crystal structures are three-dimensional and are not based on chains or sheets. The NLC effect in uranyl squarate monohydrate [6] is related to the changes of the internal geometry of uranyl coordination polyhedra under pressure and for silver oxalate to the variations of the relative distances of the silver coordination polyhedra [7]. These mechanisms are different from the majority of mechanisms used up to date to rationalize the NLC phenomenon as the ferroelastic instabilities, phonon instabilities, reverse ferroelastic phase transitions, correlated polyhedral tilts and helical and wine-rack structural motifs [20]

Since the *state of the art* of the theoretical solid state methodology is very advanced, high-quality applications performed in large scale computer installations with the appropriate methods and calculation parameters have predictive value and generally lead to material properties in good agreement with experiment [117–142]. The present computational study was carried out using very demanding calculation parameters chosen to obtain nearly converged crystal structures, energies and elastic properties with respect to these parameters and therefore must be properly reproducible. Similar computations based on accurate enough computational methods and carried out with a sufficient level of complexity associated to the calculation parameters employed should lead to essentially the same conclusions. The results of this paper should be confirmed experimentally. Due to the large availability of the materials studied and the fact that high pressure methods are well established, the verification must be a relatively easy matter from the experimental point of view.

The present work and the previous studies [1–7] suggest that many other organic and metal-organic materials could exhibit extremely anomalous negative mechanical phenomena. The possibility of discovering even larger NLC effects in these materials is very significant. Since oxalic acid [2–3] and silver oxalate [7] were previously shown to exhibit

a highly anomalous behavior, these works and the present study suggest that the mechanical properties of additional members of the group of metal oxalates should be studied in detail.

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