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Crystal and chemical anisotropy effects in AE_2ZnN_2, (AE = Ca, Sr, Ba) from ab initio

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This work is dedicated to the memory of Professor David BOHM, a great mind of all times.

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ABSTRACT

In the tetragonal ternary nitrides AE_2ZnN_2 (AE = Ca, Sr, Ba), Zn has a rare linear coordination with nitrogen (N–Zn–N) along the c axis and N is located in an AE_5Zn–like octahedron. Such features lead to original anisotropic crystal and chemical bond effects addressed herein with DFT-GGA based methods accounting for the cohesive energies, the energy volume equations of state EOS, the elastic constants and the properties of chemical bonding. Along AE = Ca, Sr, Ba an increasing overall compressibility under hydrostatic pressure is inferred from the respective EOS's, but the elastic constants C_{ij} exhibit highly anisotropic features with large magnitudes of C_{33} along the tetragonal c axis versus smaller $C_{11} = C_{22}$ along a, b. Decreasing $C_{33}-C_{11}$ along the title compounds signals decreasing anisotropy. The three ternaries are calculated as small gap insulators in agreement with experimental results of conductivity. The chemical bonding characterizes strong Zn–N bonds versus weaker AE–N thus reflecting the crystal anisotropy.

1. Introduction and context

Nitrides offer a broad range of chemical compounds with interesting physical properties mainly related with the covalent character of the bond of the host elements with nitrogen. This is illustrated for instance by the extreme hardness of light element nitrides within the B–C–N diagram such as the cubic boron nitride c-BN which replaces diamond in many tooling machines either as bulky materials or more recently as thin films [1], the ternary BC_2N [2] and the theoretically devised $C_{11}N_4$ [3]. Also the refractory character of transition metal mononitrides [4] and of SiCN ceramics [5] is of large interest in industry.

AE_2ZnN_2 (AE = Ca, Sr, Ba) ternaries were synthesized by DiSalvo group in the 1990's [6,7]. They form the first nitrides with the A_2HgO_2 (A = alkaline element) archetype prepared earlier by Hoppe and Röhrborn in 1964 [8]. The structure is body centered tetragonal with large c/a ratio of 3.1–3.5. It is characterized by a rare linear coordination of Zn to nitrogen: N...Zn...N and an *AE5Zn* irregular octahedron surrounding nitrogen with five long $d_{AE\text{-}N}$ and one short d_{Zn-N} (cf. Fig. 1). This leads to ionocovalent compounds with chemical generic formulation: $2AE^{2+}\{N...Zn...N\}^{4-}$ where ZnN_2^{4-} is a complex linear anion. The directional N...Zn...N bonds along the tetragonal c-axis are likely to exhibit original anisotropic mechanical as well as peculiar chemical bonding effects leading to specific physical properties which are examined herein by calculating the electronic structure and energy derived quantities of the three compounds within the quantum mechanical framework of the density functional theory DFT [9]. Two computational methods were used in a complementary manner. The Vienna ab initio simulation package (VASP-PAW) code [10,11] allows accurate protocols of geometry optimization, cohesive energies, energy volume equations of state (EOS) and the calculation of the complete set of elastic constants. Then a full account of the electronic structure and of the properties of chemical bonding (not implemented in VASP) is done with full potential all electrons augmented spherical wave (ASW) method [12,13]. The DFT exchange-correlation XC effects were considered following the generalized gradient approximation (GGA) according to the scheme of Perdew, Burke and Ernzerhof (PBE) [14]. Details on the methods can be found in a recent work [15] and therein references.

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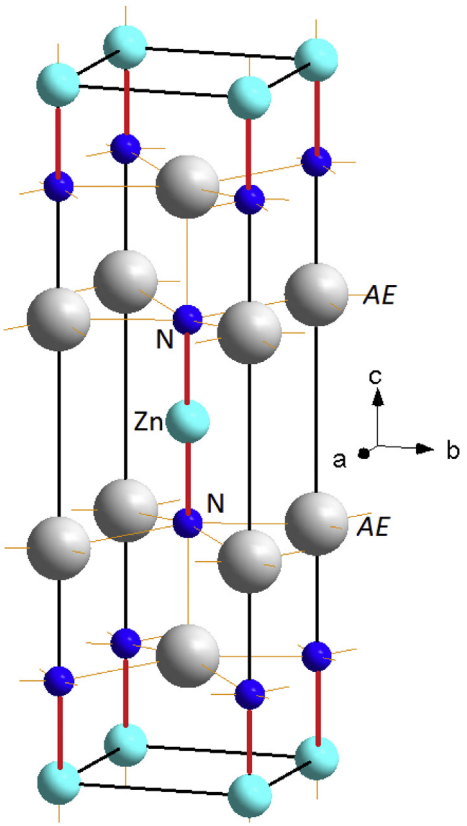

Fig. 1. Crystal structure of AE_2ZnN_2 (AE = Ca, Sr, Ba) family highlighting the linear N–Zn–N connections.

2. Geometry optimization and energy based results

2.1. Geometry optimization and cohesive energies

Starting from the experimental structure parameters of AE_2ZnN_2, AE = Ca, Sr, Ba [6,7] given in Table 1, unconstrained geometry optimization runs were carried out. In all three ternary compounds the tetragonal symmetry in $I4/mmm$ space group was preserved after successive calculations with increasing precision of the Brillouin zone integration. As shown in Table 1, the fully relaxed structure parameters are found close to the starting ones and the shortest interatomic distances are in fair agreement with experiment. The distance d(Zn–N) = 1.84 Å is almost constant throughout the series and smaller than d(AE–N) which ranges from 2.41 Å (AE = Ca), to 2.54 Å (AE = Sr) and 2.60 Å (AE = Ba) whence the volume increase (Table 1). The calculated volumes present smaller magnitudes than experimental values but it will be shown in next paragraph that a better agreement is obtained from the energy-volume equations of states (EOS) fit values (cf. Fig. 2).

The last lines of Table 1 report the total and cohesive energies. The latter are obtained from

$$E_{\text{coh.}} = E_{\text{total}}(\text{compound}) - \sum E(\text{constituents}) \text{ for one FU.}$$

The energies of the constituents were calculated in their ground state structures using available PAW-GGA potentials: FCC for AE with E_{Ca} (including p semi-core state) = −1.954 eV/atom, E_{Sr} (including s and p semi-core state) = −1.677 eV/atom, E_{Ba} (including s and p semi-core state) = −1.911 eV/atom, hexagonal E_{Zn} = −1.250 eV/atom and N_2 in a large cubic box, $E_{N2.}$ = −16.136 eV. The trend of decreasing cohesive energies along

Table 1
Calculated and experimental [6,7] (in parentheses) lattice and atomic parameters for AE_2ZnN_2, (AE = Ca, Sr, Ba). Space group $I4/mmm$ with Zn at (2a): 0, 0, 0, AE and N at (4e): 0, 0, z. Total electronic and cohesive energies are given as per formula unit (FU).

AE_2ZnN_2	AE = Ca	AE = Sr	AE = Ba
a (Å)	3.56 (3.58)	3.83 (3.86)	4.12 (4.15)
c (Å)	12.56 (12.66)	12.82 (12.93)	12.90 (13.05)
V (Å^3)	159.18 (162.26)	188.06 (192.65)	218.97 (224.75)
z_{AE}	0.303 (0.302)	0.342 (0.341)	0.348 (0.344)
z_N	0.147 (0.146)	0.144 (0.145)	0.143 (0.141)
$E_{Tot.}$ (eV)/FU	−25.47	−24.02	−23.75
$E_{coh.}$ (eV)/FU	−4.17	−3.27	−2.54

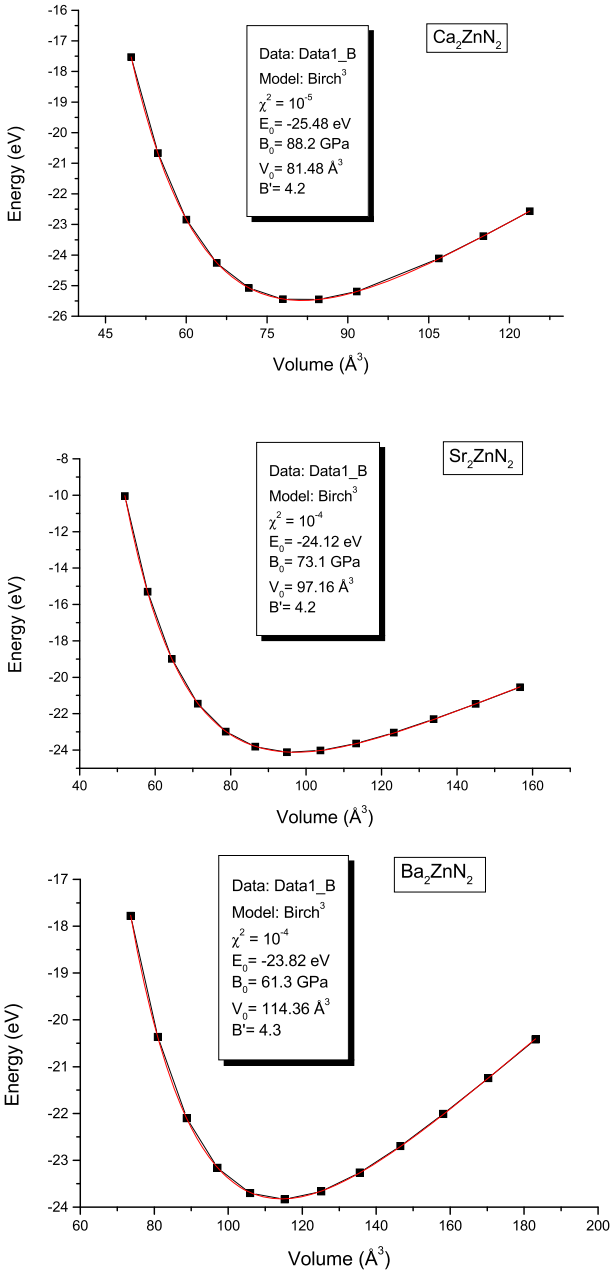

Fig. 2. AE_2ZnN_2 (AE = Ca, Sr, Ba). Energy volume curves and fit values (in the insert) from Birch 3rd order equation of state. χ^2: the goodness-of-fit.