First-Principles Study of Electronic and Vibrational Properties of BaHfN$_2$

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The transition metal nitride BaHfN$_2$, which consists of weakly bonded neutral slabs of closed shell ions, has structural and chemical similarities to other layered nitrides which have impressive superconducting T$_c$ when electron doped: $\text{A}_x\text{MNCl}$, $\text{A}_x\text{ZrNCl}$, $\text{A}_x\text{TiNCl}$, with $T_c = 25.5$, 15.2 and 16.5 K, respectively for appropriate donor (A) concentrations $x$. These similarities suggest the possibility of BaHfN$_2$ being another relatively high T$_c$ nitride upon doping, with effects of structure and the role of specific transition metal ions yet to be understood. We report first-principles electronic structure calculations for stoichiometric BaHfN$_2$ using density functional theory with plane-wave basis sets and separable dual-space Gaussian pseudopotentials. An indirect band gap of 0.8 eV was obtained and the lowest conduction band is primarily of Hf $5d$ character, similar to $\beta$-ZrNCl and $\alpha$-TiNCl. The two N sites, one in the Hf layer and another one in the Ba layer, were found to have very anisotropic Born effective charges (BEC): deviations from the formal charge (-3) are opposite for the two sites, and opposite for the twoorientations (in-plane, out of plane). LO-TO splittings and comparison of BECs and dielectric constant tensors to those of related compounds are discussed, and the effect of electron doping on the zone-center phonons is reported.

I. INTRODUCTION

High temperature superconductivity has been a puzzle since the quasi-two-dimensional, doped insulating copper oxides were reported to become superconducting with very high T$_c$'s. Since then several other layered transition metal oxides have been found to be good superconductors although at relatively low temperature, for example Li$_2$NbO$_2$ and Na$_x$CoO$_2$ at about 5 K. The undoped parent compounds of the cuprate high-temperature superconductors are magnetic insulators and their transition from a magnetic insulator to a metal upon doping completely modifies their electronic structure. These transition metal oxides still attract a great deal of interest because the superconductivity is not yet well understood.

Recently, interest has been growing for another class of layered superconductors, the transition metal nitrides such as MNX (M=Ti, Zr, Hf; X=Cl, Br, I) and ternary transition metal dinitrides AMN$_2$ (A=alkaline earth metal, M=Ti, Zr, Hf), some of which have been reported to become superconducting with high T$_c$ values. Superconductivity up to 12 K was first measured in $\beta$-ZrNCl by Yamanaka et al. in 1990, and since then the highest T$_c$'s that have been measured for these transition metal nitrides are as follows: 25.5 K for Li$_{0.48}$(THF)$_x$HfNCl$_2$, 15.2 K for intercalated $\beta$-ZrNCl, and 16.5 K recently reported for $\alpha$-TiNCl upon doping with Li. These electron-doped transition metal nitrides form a new and seemingly unconventional class of high T$_c$ superconductors because, unlike the transition metal oxides, the parent compounds are not Mott insulators. The parent compounds for these layered quasi-2D nitrides are non-magnetic ionic band insulators with a gap in the range of 2-4 eV.

In these transition metal nitrides, the superconducting mechanism presents a real conundrum. Experimental measurements of the isotope effect$^{11}$ in Li$_x$ZrNCl show a very weak dependence on the N mass, suggesting that electron-phonon mediated pairing cannot adequately account for the superconductivity in the MNX family. Specific heat measurements on Li$_x$ZrNCl$^{12}$ estimate the upper limit for the electron-phonon coupling constant $\lambda \approx 0.2$ for Li$_{0.12}$ZrNCl. A theoretical study on Li$_x$ZrNCl$^{13}$ predicted the coupling constant on the average around 0.5. The computed and the estimated coupling constant is far too small to account for the $T_c$ of 12-15 K. The magnetic susceptibility measurements$^{14}$ also give a mass enhancement factor that appears too small for electron-phonon coupling.

There is no clear evidence of strong electronic correlations in the transition metal nitrides. These compounds do not show the antiferromagnetism that is characteristic of strong correlations nor even the Curie-Weiss susceptibility that signals local moments, and there is no frustration on either the honeycomb lattice or rectangular lattice. In fact, the bandwidths of the $d$ states (where doped electrons reside) are rather large$^{15}$ and undoped systems are in $d^0$ configurations, so these systems should be well described (except for the value of the gap) by first-principle calculations employing the local density approximation (LDA). There is no observation of magnetism in the parent compounds at all, so the possibility of spin fluctuations as a pairing mechanism, similar to what is thought by some to cause su-
perconductivity in cuprates, seems unlikely. While a possible pairing mechanism mediated by magnetic fluctuations has been suggested, this mechanism seems at odds with observed behavior so far. Some groups have also proposed charge fluctuations as a pairing mechanism or plasmon enhancement of weak BCS superconductivity.

In this paper we focus on the ternary nitride BaHfN$_2$, whose electronic structure and vibrational properties have not yet been studied theoretically. This compound has many chemical and structural similarities with the layered transition metal nitrides MNCI$_2$(M=Ti,Hf,Zr) that are impressive superconductors when they are electron doped. We suggest that this compound has the potential to provide another high $T_c$ transition metal nitride superconductor when electron doped. In this paper we present calculations of the electronic structure, lattice vibrations and dielectric constant tensors of BaHfN$_2$, and compare them with those of other nitrides. This comparison with other layered nitrides may help in predicting the origin of the superconductivity in these layered nitrides.

The rest of the paper is organized as follows. We first describe the crystal structure of BaHfN$_2$ (Sec. II) and the computational methods (Sec III). Then we present our results for structural and electronic properties of BaHfN$_2$ (Sec. IV), followed by analysis of the vibrational properties (Sec. V). Finally, we discuss the case when BaHfN$_2$ is electron doped by replacing one of the two Ba atoms in the unit cell by a La atom (Sec. VI). A summary of our findings in Sec. VII concludes the paper.

II. STRUCTURE

We use structural coordinates for BaHfN$_2$ from powder X-ray diffraction measurements reported by Gregory et al. The nitrodoahafnate BaHfN$_2$ crystallizes in the tetragonal space group P4/nnm, for which KCoO$_2$ is the customary example. The measured lattice constants are $a = 4.128$ Å and $c = 8.382$ Å. There are two inequivalent N sites which we denote N1 (lying nearly in the Hf plane) and N2 (nearly in the Ba plane), i.e. BaN$_2$-HfN1. Ba, Hf and N2 occupy Wyckoff position 2c ($\frac{1}{2}$, $\frac{1}{2}$, $z$) and N1 occupies position 2b ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (see Table I).

The structure of BaHfN$_2$ shown in Fig. 1 is sometimes described as composed of [HfN$_5$]$^{2-}$ anions and Ba$^{2+}$ cations. These anions are composed of Hf atoms inside a square pyramid of 5 nitrogen atoms (four N1’s and one N2), forming layers of edge sharing pyramids stacked along the c axis; the apices of adjoining pyramids are aligned alternatively up and down along the c axis. The Ba$^{2+}$ cations are situated between these Hf-N sheets levelled with the pyramid apices.

Another description for the structure of BaHfN$_2$ comprises of (nearly) coplanar (BaN$_2$)$^-$ layer and a corrugated (HfN1)$^+$ layer, with Hf ions lying alternately above and below the N2 layer. Each neutral BaN$_2$-HfN1-NHf-N2Ba structural unit (outlined in Fig. 1) is weakly bonded to neighboring units in the $c$ direction; upon intercalation, dopant ions will lie between the Ba-N2 layers. Similarly, in $\alpha$-TiNCl (Fig. 1b) there is a layer of transition metal (Ti) atoms and N atoms, with Cl$^-$ ions playing a role analogous to the (BaN$_2$)$^-$ unit in BaHfN$_2$. Neutral TiNCl slabs are weakly bound to each other. A more detailed study of that compound will be presented separately.

As we show below, the site energies and bonding of the N1 and N2 sites are quite different, and the simple viewpoint of formal closed shell ions, e.g. Ba$^{2+}$, Hf$^{4+}$, N$^{3-}$ may not be sufficient to address the structural relationships.

III. DESCRIPTION OF CALCULATIONS

We carried out density functional theory (DFT) calculations with the ABINIT package, within both local density approximation (LDA) and gradient corrected (GGA/PBE) exchange and correlation functionals. Norm-conserving pseudopotentials (PSPs) in the relativistic separable dual-space Gaussian Hartwigsen-Goedecker-Hutter (GHH) form were used to treat the electronic configuration of Ba ($5s$, $5p$, $6s$), Hf ($5s$, $5p$, $5d$, $6s$) and N ($2s$, $2p$), including $5s$, $5p$ semi-core states for Ba and Hf. Plane wave basis sets with a kinetic energy cutoff of 120 Ry were used. A 8 \times 8 \times 4 Monkorst-Pack $k$-point grids were used to sample the Brillouin zone for ground state calculations. We have checked that further increasing the cutoff energy to 140 Ry or the $k$-point grid to 12 \times 12 \times 6 and 18 \times 18 \times 6 has a negligible influence on the relaxed geometry and phonon frequencies. The computed LDA band structure of BaHfN$_2$ at experimental geometry was found to agree well with results obtained from the full-potential, all electron code FPLO; the latter also provides a convenient way to compute contributions to the electronic bands and density of states from individual atomic orbitals. We have confirmed that spin-orbit coupling has no significant influence on the band structure. Phonon calculations are carried out at the $\Gamma$ point, and the obtained frequencies and displacement eigenmodes were used to compute Born effective charges and the static dielectric tensor $\varepsilon_0$.

To examine the influence of PSPs on the cal-


FIG. 1. (Color online) (a) Layered geometry of BaHfN$_2$: N$^{3-}$ anions form a square base pyramid around Hf$^{4+}$, forming a [HfN$_2$]$^{2-}$ anion. Ba$^{2+}$ cations sit in between the tips of the pyramids. (b) Layered $\alpha$-TiNCl structure.

TABLE I. Structurally optimized lattice constants ($a$ and $c$) and reduced internal coordinates ($z$) for atoms in the unit cell, obtained from different sets of pseudopotentials (PSPs) including Hartwigsen-Goedecker-Hutter (HGH)\textsuperscript{19,20} and Troullier-Martin (TM)\textsuperscript{21} type PSPs. The inclusion of semicore 5$s$ and 5$p$ states for Ba and Hf PSPs are indicated by Ba$^{sc}$ and Hf$^{sc}$ respectively. The computed band gap for the experimental geometry, $E_{\text{exp}}$, is compared with FPLO (FLAPW) results.

| PSP           | $a/a_{\text{exp}}$ | $c/c_{\text{exp}}$ | $z$(Ba) | $z$(Hf) | $z$(N2) | $E_{\text{exp}}^g$ (eV) |
|---------------|---------------------|---------------------|--------|--------|--------|---------------------|
| LDA FPLO      | 0.992               | 0.986               | 0.846  | 0.415  | 0.177  | 0.68                |
| FLAPW         |                     |                     |        |        |        | 0.8                 |
| HGH, Ba$^{sc}$, Hf$^{sc}$ | 0.986               | 0.982               | 0.848  | 0.415  | 0.176  | 0.82                |
| TM            | 1.005               | 1.017               | 0.846  | 0.415  | 0.177  | 0.78                |
| TM, Ba$^{sc}$ | 0.997               | 0.987               | 0.849  | 0.413  | 0.170  | 0.87                |
| TM, Ba$^{sc}$, Hf$^{sc}$ | 0.984               | 0.972               | 0.847  | 0.415  | 0.177  | 1.11                |
| PBE HGH, Ba$^{sc}$, Hf$^{sc}$ | 1.000               | 1.007               | 0.848  | 0.415  | 0.180  | 0.95                |
| TM            | 1.022               | 1.036               | 0.845  | 0.416  | 0.186  | 1.00                |
| TM, Ba$^{sc}$ | 1.011               | 1.008               | 0.850  | 0.413  | 0.175  | 1.13                |
| TM, Ba$^{sc}$, Hf$^{sc}$ | 1.004               | 0.999               | 0.849  | 0.414  | 0.179  | 1.25                |
| Exp$^2$       |                     |                     |        |        |        | 0.8479 0.4142 0.168 |

Calculated structural, electronic and vibrational properties of BaHfN$_2$, especially the inclusion of 5$s$, 5$p$ semicore states for Ba and Hf, we also carried DFT calculations using Troullier-Martin (TM)\textsuperscript{22} PSPs generated using the fhi98PP program\textsuperscript{26} with LDA/PZ\textsuperscript{27} and GGA/PBE exchange-correlation functionals, respectively. A 8×8×4 $k$-grid and a kinetic energy cut-off of 90 Ry were used.

To simulate the doped BaHfN$_2$, we replaced one of the two Ba atoms in the unit cell with La, which provides an extra electron per formula unit and provides metallic screening with its impact on the zone-center phonons. The HGH PSPs were used to do calculations for the doped system with kinetic energy cut-off of 120 Ry and and a k-point mesh of 12×12×6.

IV. ELECTRONIC STRUCTURE CALCULATIONS

A. Structural Relaxation and Electronic Structure

It is instructive for future studies to quantify the effects of different types of pseudopotentials on the relaxed structure and the energy gap. We have performed structural relaxation for the BaHfN$_2$ crystal using both LDA and GGA/PBE, and results are compared with experimental geometry\textsuperscript{5} in Table I. In addition to the HGH PSPs, we also employed different sets of norm-conserving TM PSPs. The inclusion of 5$s$ and 5$p$ semicore states, if present, is denoted by Ba$^{sc}$ and Hf$^{sc}$ respectively. The optimized cell parameters and internal coordinates were
compared with all-electron, full potential reference results from FPLO. The band gap was computed for the experimental geometry, $E_{\text{exp}}$ using FPLO and full potential linear augmented plane waves code (FP-LAPW) implemented in the Elk code. The results are listed in Table I.

One observation from Table I is that as one includes semicore states of Ba and Hf, the equilibrium lattice constants becomes smaller, while the energy gap $E_{\text{exp}}$ increases substantially. Such trend holds for both LDA and PBE PSPs of TM type. The inclusion of semi-core states is important since there is significant amount of hybridization of Ba semi-core 5p states with N2 2s state, as can be seen from Fig. 2. We observed a trend of decrease in equilibrium lattice constants upon inclusion of semi-core states. This is mainly due to the decrease of Ba-N2 and Ba-Hf bond length.

On the other hand, TM-type PSPs generated using the fhi98PP code are so-called single projector pseudopotentials, e.g. there is only one pseudopotential for each angular momentum type, not for each valence orbital. The corresponding PSPs with Ba$^{4+}$ and/or Hf$^{4+}$ failed to describe the energy position of 6s states properly, even for the isolated atoms. Such PSPs tend to predict energy gaps of BaHfN$_2$ larger than those without the semicore states in the valence configuration. The discrepancy in $E_{\text{exp}}$ compared with all-electron calculations can be as much as 0.4 eV. The HGH pseudopotentials, on the other hand, were constructed with multiple projectors per angular momentum type and therefore can describe orbitals of same angular momentum but different shells reasonably well. Indeed, from Table I we find that overall HGH pseudopotentials give structural properties and energy gap similar to those calculated from all-electron calculation and in the following, we present results obtained with LDA type HGH pseudopotentials.

Equation 1 shows the band structure of BaHfN$_2$, using the so-called fatbands emphasis of band character for Hf 5d$_{xy}$ states. The fatbands are obtained by using the expansion of the wavefunctions in terms of the basis atomic orbitals at each k-point

$$|k_n\rangle = \sum_{R,s} c_{L,s}^{n} e^{i\mathbf{R}\cdot\mathbf{s}} \langle \mathbf{R} | s \rangle |L \rangle,$$

where $n$ is the band index and $L \equiv lm$ is the orbital index. $\mathbf{R} + s$ denotes a regular lattice site, with $\mathbf{R}$ a Bravais lattice vector and $s$ a basis vector of the unit cell. The width of the fatband is proportional to $|c_{L,s}^{n}|^2$.

BaHfN$_2$ is a band insulator with a calculated band gap 0.68-0.80 eV using full-potential, all-electron methods (FPLO, LAPW). Given the usual LDA underestimate of band gaps the true gap of BaHfN$_2$ may be as large as 1.5 eV. This layered ionic semiconductor character is very similar to that of the MNCi compounds (M=Ti, Hf, Zr) which have been found to superconduct with impressively high $T_c$ values when electron-doped. The lowest conduction band in BaHfN$_2$ has primarily Hf 5d$_{xy}$ character with a width of 3 eV. Since these states are empty, Hf is formally 4+, and the rest of the electronic structure is indicative of a closed shell, ionic insulator with some mixing of N 2p states and Hf 5d states. This characterization is similar to ZrNCl, which is...
also an ionic semiconductor with lowest conduction band having Zr in-plane 4d character and TiNCl which has Ti 3d_{xy} character. The Hf 5d character extends through a range of 8 eV beyond the Fermi level (see Fig. 2b) partially due to crystal field splitting of the 5d orbitals.

Figure 4 shows the projected density of states in the valence-conduction band region. Integrating the density of states, we find that only above a doping concentration x = 0.17 for doping concentration x when doped with alkali metals; for doping concentration x > 0.17 carriers also go into the bottom of the Ba 5d bands at M and then additional Hf 5d bands at \( \Gamma \). In this respect, BaHfN\(_2\) is similar to TiNCl\(_2\), but different from the hexagonal compounds [(Zr,Hf)NCl] which have the band minimum at the zone corner K points, of which there are two.

This difference in Fermi surfaces has some importance for electronic response. In the doped (Zr,Hf)NCl compounds, nesting of the two Fermi surfaces has recently been put forward as a potential source of spin fluctuations, which was suggested as a possible candidate for pairing mechanism. However, with a single simple Fermi surface such as displayed by doped TiNCl (known to be an excellent superconductor) and doped BaHfN\(_2\) (which we suggest by analogy may be a good superconductor), this mechanism is not available. Since the superconducting \( T_c \) is large (and almost similar in magnitude) in TiNCl and ZrNCl, and their characters are otherwise so similar but Fermi surfaces are different, the mechanism of spin fluctuations seems to be degraded in likelihood. Electron-phonon coupling is weak in A\(_2\)ZrNCl, and the materials are pauli-paramagnetic. Thus for possible pairing in these materials, long sought electronic mechanisms of pairing need consideration. A single electron gas with a given value of \( k_F \) is different from a pair of identical, degenerate electron gases with a value of \( k_F \) that is \( 1/\sqrt{2} \) as large. One main difference, as mentioned above, is that there is no nesting that might enhance charge fluctuations (as is the case also for spin fluctuations) or affect pairing symmetry. Another clear difference is that the characteristic momentum scale \( k_F \) is different.

V. VIBRATIONAL SPECTRUM

A. Born-Effective Charges

The MNCl compounds become superconducting upon electron doping from an ionic insulator to the metallic phase. The relatively low density electron gas that is formed upon light doping might not adequately screen the ionic nature of the MN layers, so the electronic response may still have short-range ionic character. For this reason we calculate and
analyze the Born effective charges in some detail.

The Born effective charge (BEC) tensor \( Z^* \) is a fundamental quantity for the study of lattice dynamics, describing the long range Coulomb part of the tric field, or as the force that would induce on atom \( \kappa \) the periodic displacement \( \tau_{\kappa,\alpha} \) under the condition of zero macroscopic electric field, and as the force \( F_{\kappa,\alpha} \) induced on atom \( \kappa \) by an electric field \( \varepsilon_{\gamma} \) under the condition of no atomic displacement. It can also be expressed as the second partial derivative of the total energy with respect to the displacement and the electric field:

\[
Z_{\kappa,\gamma\alpha}^* = V \frac{\partial P_{\gamma}}{\partial \tau_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial \varepsilon_{\gamma}} = - \frac{\partial^2 E}{\partial \varepsilon_{\gamma} \partial \tau_{\kappa,\alpha}} \tag{2}
\]

where \( V \) is the volume of the unit cell. One might naively expect the BECs to be close to the formal charges of the compound, but this is often not the case. The BEC can be decomposed into the charge of the (pseudo-) ion \( \kappa, Z_{\kappa} \), and the electronic screening term, \( \Delta Z_{\kappa,\gamma\alpha} \).

\[
Z_{\kappa,\gamma\alpha}^* = Z_{\kappa,\gamma\alpha} + \Delta Z_{\kappa,\gamma\alpha} \tag{3}
\]

The computed BECs for BaHfN\(_2\) are provided in Table II. In tetragonal symmetry the BEC tensor is diagonal and reduces to two values \( Z_{xx}^* = Z_{yy}^* \) and \( Z_{zz}^* \). The BECs for Hf and Ba in the plane are reasonably close to their formal charges (Hf is 0.52 larger and Ba is 0.73 larger), while their perpendicular charges differ substantially from the formal charges (being smaller than the formal charge for Hf) indicating a more complex electronic response.

The two nitrogen sites have very different and unusual BECs. For comparison, previously calculated\(^{22}\) BECs of NaCoO\(_2\) are also listed in Table II. The BECs for O in NaCoO\(_2\) are rather uninteresting, both being smaller than their respective formal charges. By contrast, in BaHfN\(_2\), N1 has a BEC of -4.66 in the plane and -1.65 perpendicular to the plane, respectively with magnitude much larger and much smaller than the formal charge. N2, on the other hand, has a BEC of -2.6 in the plane and about -4.6 perpendicular to the plane, again very different from the formal charge but in the opposite sense with respect to N1. The BEC of N1 is consistent with covalent bonding between N1 and Hf, given its anomalously large magnitude in the plane. N2 behaves in the opposite way, and its BEC is consistent with little covalent bonding with Ba (as expected) but with significant covalent interaction with Hf in the inner layer. BECs with magnitudes greater than the formal charges reflect large electronic response to atomic motion. For example, in the case of pervoskite BaHfO\(_3\), the large Born-effective charges of Hf (\( Z^* = 5.75 \)) and O (\( Z^*_{O_{\parallel}} = -4.42, Z^*_{O_{\perp}} = -2.03 \)) indicate a mixed ionic-covalent nature of Hf-O bond, similar to the case found here for the Hf-N1 bond. Also, Ba in BaHfO\(_3\), which has a cubic site symmetry, was found to have a similar average BEC (\( Z^* = 2.72 \) as that computed for Ba in BaHfN\(_2\) here (\( Z^* = 2.87 \)).

The Hf-N1 layer, taken as a unit, behaves as if having a charge of -0.14 (nearly neutral) in the plane and +1.44 (slightly cationic, rather consistent with the formal charges) for vibrations perpendicular to the plane. The Ba-N2 layer behaves in an opposite manner.

In Table III we draw a comparison between the BECs of metallochloronitrides MNCl (M=Ti, Hf, Zr)\(^{33}\) and those of MNCl (M=Ti, Hf, Zr)\(^{28}\) show similar trends as do the BECs of N1 in BaHfN\(_2\) and the N in MNCl. There is considerable anisotropy in the effective charges for both the M and N ions. The effective charge for Cl in MNCl is close to its formal charge (reflecting its high electronegativity), however the Cl analog in BaHfN\(_2\), Ba-N2, is somewhat different, with large anisotropy.

### B. Zone-Center Phonons

BaHfN\(_2\) has 8 atoms in the unit cell resulting in 24 phonon modes, three of which are acoustic modes and the remaining 21 are optical modes. The phonon frequencies are listed in Table III with their polarization and symmetry. There are 8 \( E_g \) and 6 \( E_u \) modes with polarization perpendicular to the \( c \) axis (within the \( x-y \) plane) and 3 \( A_{1g} \) and 3 \( A_{2u} \) modes with polarization along the \( z \) axis. The modes \( A_{1g} \), \( B_{1g} \), \( E_g \) are Raman active, and the modes \( A_{2u} \), \( E_u \) are...
TABLE III. Calculated zone-center phonon frequencies for BaHIn$_2$ and Ba$_{0.5}$La$_{0.5}$HIn$_2$. The phonons were computed using the optimized geometry. All phonons with $x$-$y$ polarization are doubly-degenerate. The symmetry column refers to the symmetry of the phonons in higher symmetry insulating system (point group $D_{4h}$ vs. $C_{4v}$ for the metallic system). There is a split in degeneracy in the long wavelength limit between the LO and TO modes, and the magnitude of LO-TO splitting, $\sqrt{\omega^2_{TO} - \omega^2_{LO}}$, is listed in the last column. All frequencies reported in cm$^{-1}$.

| Mode | Symmetry | Polarization | BaHIn$_2$ frequency $\omega_{LO}$ | $\omega_{TO}$ | Ba$_{0.5}$La$_{0.5}$HIn$_2$ frequency $\sqrt{\omega^2_{TO} - \omega^2_{LO}}$ |
|-------|-----------|--------------|----------------------------------|-------------|------------------------------------------|
| 1-2$^b$ | $E_u$     | $x$-$y$      | 72                               | 93          | 59                                       |
| 3-4$^b$ | $E_g$     | $x$-$y$      | 82                               | 94          |
| 5$^b$   | $A_{2u}$  | $z$          | 105                              | 144         | 144                                      |
| 6$^b$   | $A_{1g}$  | $z$          | 120                              | 136         |
| 7-8$^b$ | $E_g$     | $x$-$y$      | 152                              | 148         |
| 9$^b$   | $A_{1g}$  | $z$          | 172                              | 175         |
| 10-11$^b$ | $E_u$   | $x$-$y$      | 210                              | 240         | 116                                      |
| 12-13$^b$ | $E_g$   | $x$-$y$      | 232                              | 283         |
| 14$^b$  | $B_{1g}$  | $z$          | 341                              | 328         |
| 15-16$^b$ | $E_u$   | $x$-$y$      | 424                              | 614         | 444                                      |
| 17$^b$  | $A_{2u}$  | $z$          | 466                              | 492         | 152                                      |
| 18-19$^b$ | $E_g$   | $x$-$y$      | 623                              | 651         |
| 20$^b$  | $A_{2u}$  | $z$          | 641                              | 751         | 391                                      |
| 21$^b$  | $A_{1g}$  | $z$          | 717                              | 646         |

$^a$ IR active mode
$^b$ Raman active mode

infrared active. We found some phonon frequencies were quite sensitive to the inclusion of semi-core states in Ba and Hf pseudopotentials with several phonons differing by 15-30% in the absence of semi-core states.

The LO-TO splittings of the IR active modes can be related to the Born-effective charges as

$$\sum_m \left[ \omega^2_{LO,m} - \omega^2_{TO,m} \right] = \frac{4\pi}{\epsilon^{\infty}_{\alpha\alpha} V} \sum_\kappa \left( \epsilon Z^*_\kappa,\alpha \right)^2 M_\kappa. \quad (4)$$

In this relation, $m$ goes over the IR active modes of a given polarization direction $\alpha$, $M_\kappa$ is the ionic mass of the atom $\kappa$, and $\epsilon Z^*_\kappa,\alpha$ is the $\alpha$-th diagonal element of the high frequency dielectric constant. When the LO phonons are excited, a macroscopic electric field is created due to the long range nature of the Coulomb interaction. The squares of the BECs, divided by the mass, give the contribution of that ion to the electric field. One interesting example (see Table III): the large splitting $\Delta \omega$ of mode 15 is due largely to the fact that the light N1 ions are vibrating in the $x$-$y$ plane and the BEC for N1 is rather large ($-4.66$), accounting for most of the shift of 45% in LO frequency. The second largest splitting $\Delta \omega$ is for the mode 20, with a shift of about 17% in frequency. In this mode we have primarily N2 vibrating along the z direction and the BEC for N2 along z is $Z^*_{zz}(N2) = -4.58$ which again accounts for the large splitting. Mode 5 has a large relative shift of 37%; it has primarily N1 and Ba vibrations opposite to each other.

TABLE IV. Calculated macroscopic dielectric constants for BaHIn$_2$ and group IVB nitrochlorides using (a) fully relaxed geometry and (b) the experimental structure with relaxed atomic positions.

| Mode | $\epsilon_{xx/yy}^\infty$ | $\epsilon_{zz}^\infty$ | $\epsilon_{zz/yy}^\infty$ | $\epsilon_{xx/zz}^\infty$ |
|-------|--------------------------|-----------------------|--------------------------|--------------------------|
| (a) BaHIn$_2$ | 7.47                     | 7.35                  | 33.8                     | 21.4                     |
| (b) BaHIn$_2$ | 7.35                     | 7.31                  | 44.7                     | 24.0                     |
| (b) $\alpha$-TiNCl | 6.9/7.4                | 3.2                   | 22.3/38.3                | 3.7                     |
| (b) $\beta$-ZrNCl | 6.2                     | 4.4                   | 13.8                     | 5.9                     |
| (b) $\beta$-HfNCl | 5.4                     | 4.0                   | 11.1                     | 5.1                     |

$\omega_{TO}$ (cm$^{-1}$) $\quad 4\pi P^M_{m,xx}$ $\quad 4\pi P^M_{m,zz}$

| Mode | $\omega_{TO}$ (cm$^{-1}$) | $4\pi P^M_{m,xx}$ | $4\pi P^M_{m,zz}$ |
|-------|--------------------------|------------------|------------------|
| 1-2   | 72                       | 14.0             |                  |
| 5     | 105                      |                  | 10.1             |
| 10-11 | 210                      | 5.1              |                  |
| 15-16 | 424                      | 7.3              |                  |
| 17    | 468                      | 1.3              |                  |
| 20    | 641                      | 2.4              |                  |
C. Dielectric Response

We now discuss the electronic and ionic lattice contributions to the macroscopic dielectric constants, computed for BaHfN₂ by doing the phonon calculation using both experimental lattice constants with relaxed geometry and completely relaxed geometry. \( \varepsilon^{\infty} \) denotes the high frequency electronic response where there is no contribution from the ionic lattice polarizability \( (P^{\text{ion}}) \) and \( \varepsilon^0 \) is the sum of the electronic and ionic response. Their relationship is given by

\[
\varepsilon_{\alpha\beta}^0 = \varepsilon^e + 4\pi P^{\text{ion}} = \varepsilon^{\infty} + 4\pi \sum_m P_{m,\alpha\beta} \tag{5}
\]

where the sum is over all the modes and \( S_{m,\alpha\beta} \) is the mode-oscillator strength tensor which is defined as

\[
S_{m,\alpha\beta} = \sum_{\kappa,\alpha'} Z^*_{\kappa,\alpha\alpha'} U_m(\kappa,\alpha') \times \sum_{\kappa',\beta'} Z_{\kappa',\beta\beta'} U_m(\kappa',\beta'), \tag{7}
\]

where \( U_m(\kappa,\alpha) \) is the component of the phonon eigenvector for the \( m \)-th mode corresponding to the displacement of atom \( \kappa \) in direction \( \alpha \).

The values of the static dielectric constants for BaHfN₂ and comparison to the group IVB metallochloronitrides, are given in Table IV. \( \varepsilon^{\infty} \) for BaHfN₂ is larger than the others for metallochloronitrides - the electronic polarizability \( \varepsilon^{\infty} \) for BaHfN₂ is larger than \( \varepsilon^{\infty} \) larger than the Hf counterpart, consistent with the smaller band gap (0.8 eV versus around 1.8 eV for ZrNCl and HfNCl).

With the exception of the in-plane values for TiNCl, the lattice polarizability \( \varepsilon^0 - \varepsilon^{\infty} \) of other MNCl’s is smaller by a factor of 5-15 relative to that of BaHfN₂. This is due to the fact that the phonons in BaHfN₂ are softer than the phonons in MNCl’s and the oscillator strengths for modes which contribute to \( P^{\text{ion}} \) in BaHfN₂ are much larger than the modes contributing \( P^{\text{ion}} \) for the other chloronitrides.

The phonon frequencies for the metallic system are shown in Table III. Although the replacement of one Ba with La changes the symmetry, corresponding modes between the two systems can be identified by examining the scalar products of their eigenvectors. Several of the softer modes have slightly higher \( \varepsilon^0 \) frequencies in (BaLa)₂HfN₂ than in BaHfN₂. These surfaces have significant three-dimensional character, but even at this level they do not reach the top of the zone (the A point). The lowering of the bands around M is also seen within the virtual crystal approximation (where both Ba and La are replaced by an ‘average ion’) so we expect this to be a robust feature for doping by La. A small Fermi surface near M, of mainly La 5d₂ character, arises near this level of doping.

The phonon frequencies for the metallic system are shown in Table IV. Although the replacement of one Ba with La changes the symmetry, corresponding modes between the two systems can be identified by examining the scalar products of their eigenvectors. Several of the softer modes have slightly higher frequencies in (BaLa)₂HfN₂ due to the decreased lattice constant of the metallic system. More interestingly, several of the high frequency modes are renormalized in the metallic system. These high frequency modes are dominated by motion of the N1 and N2 atoms.

VI. DOPING WITH ELECTRONS

We consider La substitutional doping by replacing one Ba in the unit cell with La. The vibrational frequencies for the doped system are included in Table III. Since there is no experimental data on Ba₂La₀.₅HfN₂ we use relaxed lattice constants, which are smaller by almost 3% than the experimental lattice constants of BaHfN₂. The band structure of (BaLa)₀.₅HfN₂ is shown in Fig. 5 with fat bands for Hf and La. The band structure for BaLa is 4f states are located 1 eV above \( E_F \) but have no clear impact on what we discuss in the following. There are two nearly cylindrical Fermi surfaces around \( \Gamma \), one of which has Hf 5dₓᵧ character and another has La 5dₓ₋ₜᵧ character; mixing may occur at or near crossing of the Fermi surfaces. The lowest conduction bands near \( M \), primarily La 5dₓᵧ, 5dₓ₋ₜᵧ in character (not shown as fatbands) are significantly lowered from the corresponding undoped Ba bands, creating two Fermi surfaces that are larger than anticipated from a rigid band picture using the BaHfN₂ bands. These surfaces have significant three dimensional character, but even at this level they do not reach the top of the zone (the A point). The lowering of the bands around M is also seen within the virtual crystal approximation (where both Ba and La are replaced by an ‘average ion’) so we expect this to be a robust feature for doping by La. A small Fermi surface near M, of mainly La 5dₓ character, arises near this level of doping.

VII. SUMMARY

We have examined the electronic and vibrational structure of the ternary nitride BaHfN₂ within density functional theory. We find that BaHfN₂ seems to have chemical and electronic similarities with...
high $T_c$ metallochloronitriles MNCl’s (M=Ti, Hf, Zr), so its candidacy as another high $T_c$ superconducting nitride is plausible. The basic electronic and vibrational properties of the undoped insulating phase provide a basis for an understanding of the behavior of BaHfN$_2$ upon doping. We find highly anisotropic Born effective charges for the N ions, with anisotropies that have an opposite sign for the two N sites. These differences suggest unusual electronic screening. We also provided initial analysis of how the system is affected by doping and found that bands near M are significantly lowered so that conduction would occur both in the Hf states near $\Gamma$ and in states near M located in the BaN layer.

The MNCl compounds, which are impressive superconductors when doped, provide an interesting analogy to BaHfN$_2$, with its similar structural, electronic, and vibrational similarities but larger electronic screening. One potentially important difference is worth noting. From the point of view of vapor phase growth of the materials, MNCl contain two cations – is attractive for vapor phase growth, with one electronegative anion but several cations. From this viewpoint, BaHfN$_2$ – with one anion and two cations – is attractive for vapor phase growth, and hence for study and potential application of ultra-thin superconducting layers.

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Appendix A: Description of the vibrational modes

Here we provide a brief characterization of the eigenvectors of all optical modes at $q = 0$, which can be useful in interpreting optical data and in comparing with similar ionic semiconductors. The units are cm$^{-1}$.

- $\omega=72$: Ba oscillating against other atoms in the $x$-$y$ plane. These two degenerate soft mode is largely responsible for the large static dielectric constant $\epsilon_{xx/yy}^0$.
- $\omega=82$: This mode is primarily out-of-phase Ba vibrations in the $x$-$y$ plane.
- $\omega=105$: Ba and N1 moving against each other with strong amplitude along the $z$ axis. Hf and N2 are in phase with each other oscillating weakly as compared to Ba and N1.
- $\omega=120$: This mode is primarily out-of-phase Ba vibrations along the $z$ axis.
- $\omega=152$: This mode has primarily N2 and Hf vibrations in the $x$-$y$ plane with N2 vibrating with a large amplitude as compared to Hf with Ba and N1 participating very weakly.
- $\omega=172$: Hf and N2 vibrating along $z$, with Ba vibrating very weakly opposite to Hf.
- $\omega=210$: These two mode are primarily in-phase N2 vibrations in the $x$-$y$ plane.
- $\omega=232$: These two modes are primarily out-of-phase N2 vibrations in the $x$-$y$ plane.
- $\omega=341$: This mode exhibits pure N1 vibrations along the $z$ axis, with nearest neighbor N1 atoms out of phase.
- $\omega=424$: These two modes have primarily in-phase N1 vibrations in the $x$-$y$ plane with Hf moving weakly against N1 and Ba and N2 in the Ba-N2 moving weakly in phase with N1.
- $\omega=468$: N1 vibrating with large amplitude in phase with Ba, N2 and out of phase with Hf along.

![Doped band structure showing La and Hf 5d bands. The amount of Hf 5d$_{xy}$ and La 5d$_{x^2−y^2}$ character is shown in the band structure by the weight of the points in the lines. The lowering of the 5d character due to replacement of Ba by La is substantial. The Fermi level lies at an energy of 0 eV.](image-url)
the z axis and each of the other atoms participate very weakly.

\( \omega = 623 \) : These two modes are primarily out-of-phase N1 vibrations in the x-y plane.

\( \omega = 641 \) : This mode is primarily in-phase N2 vibrations against other atoms along the z axis. This mode dominates the ionic response in the z direction, especially due to the large magnitude of BEC for N2: 

\[ Z_{zz}^\ast (N2) = -4.58. \]

\( \omega = 717 \) : This mode is primarily out-of-phase N2 vibrations along the z axis with very weak participation from Ba and Hf.

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