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Ab initio approach to cohesive properties of GdN

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We apply *ab initio* quantum-chemical methods to calculate correlation effects on cohesive properties of GdN, thereby extending the recently proposed incremental method to rare-earth compounds. Our calculated values are in reasonable agreement with the experimental cohesive energy (86.0%) and the experimental lattice constant (102.0%). Furthermore, we calculate a bulk modulus of 140.3 GPa. Taking into account estimates for the effect of a better basis both at the one-particle level and at the many-particle level, we even reach 98.5% of the experimental cohesive energy and 101.3% of the experimental lattice constant. For this estimate, we obtain a bulk modulus of 163.8 GPa. [S0163-1829(98)07304-4]

I. INTRODUCTION

During the last decade, Hartree-Fock (HF) calculations have become possible for infinite periodic systems such as polymers or solids including surfaces. An available program package is CRYSTAL.[1–4] However, the problem of an *ab initio* treatment of electron correlations in these systems has only partially been solved.[5] The incremental method[6–15] combines HF calculations for periodic systems with correlation calculations on corresponding finite clusters. In a series of papers, this computational scheme has proven to be an accurate method for the computation of cohesive properties of semiconductors[6–12] as well as ionic solids.[13–15] It competes with density-functional theory (DFT) or more precisely with approximations of DFT like the local-density approximation or improved versions employing generalized gradient approximation corrections. However, improvement toward the exact results is not as straightforward in DFT as it is in wave-function-oriented approaches such as the incremental scheme. The improvement of wave-function-based calculations is done by improving the basis set at the one- and many-particle levels. The price is an increase in the computational effort. In DFT, improvement can be attained by basic functional development aiming at a derivation of the exact functional. Although not yet suitable for routine applications, many promising approaches exist. Some of them can be found in Ref. 16.

The current work is the first application of the incremental scheme to compounds containing $4f$ elements, to our knowledge. Among the $4f$ element compounds, gadolinium-nitride GdN is one of the favorable cases featuring a lanthanide ion with a half-filled $4f$ shell and an essentially fixed valency. Still, an explicit treatment of the $4f$ shell causes severe problems in *ab initio* calculations.[17] Assuming a fixed Gd valency of three [Gd(III)], a corelike treatment of the f electrons becomes possible,[18] e.g., similar to that recently suggested in Ref. 19 within DFT. It is even possible to simulate such a core by pseudopotentials.[18] The reliability of pseudopotential calculations, including the open $4f$ shells in the core, has been demonstrated in numerous molecular applications.[17] The price we have to pay for this simplification evidently is that we can only calculate the cohesive properties for Gd in a $4f^7$ subconfiguration which is averaged over all possible intraatomic and interatomic couplings—the magnetic coupling between the gadolinium ions in the solid which is also a very interesting issue to study is neglected. Work is underway in our laboratory to account for these missing effects.

The organization of this paper is as follows. In Sec. II, we briefly describe the incremental scheme, the pseudopotentials, and the one-particle basis sets. The results are discussed in Sec. III, along with comments on the convergence of our expansion of the correlation energy. The conclusions are given in Sec. IV.

II. METHOD

In this section we describe the method and computational details. Our approach relies on two separate steps: first, we calculate the Hartree-Fock (HF) total energy using the periodic HF program package CRYSTAL.[1–4] In a second independent step we use the general framework of the incremental method[6–15] in connection with the size-extensive coupled-cluster method up to double excitations. We expand the correlation energy of the crystal into local energy increments which are evaluated in cluster calculations using the MOLPRO *ab initio* program system.[20–22] First, we briefly sketch the general features of this scheme. Afterwards, we give a detailed account of the used clusters, pseudopotentials and one-particle basis sets. Of course, all the basis sets and pseudopotentials are available from the authors upon request.

A. Incremental scheme

Given a set S of occupied one-electron orbitals, e.g., a set of localized orbitals obtained from a Hartree-Fock wave function, it is usually possible to partition this set such that electron correlations between different subsets are small. Making use of this feature, the incremental scheme is based on an expansion of the correlation energy in one-, two-, three-, . . . body increments according to the number of subsets (bodies) treated. In the present investigation the subsets refer to different ionic sites (Gd^{3+} or N^{3-}), but they can also refer to different bonds in covalent solids or other partitions, instead. A first approximation to the correlation energy of S is then the sum of all one-body increments, i.e., the correlation energies ε_i of the single subsets:

$$E^{(1)}_{\mathrm{corr},S}=\sum_{i\epsilon S}\varepsilon_i\,. \tag{1}$$

The nonadditive part of the two-body correlation energy ε_{ij}, with subsets i and j simultaneously correlated, is simply

$$\Delta\varepsilon_{ij}=\varepsilon_{ij}-\varepsilon_i-\varepsilon_j\,. \tag{2}$$

Summation of the two-body increments gives the second-order contribution to the correlation energy of S according to

$$E^{(2)}_{\mathrm{corr},S}=\sum_{i<j\epsilon S}\Delta\varepsilon_{ij}\,. \tag{3}$$

The third-order contribution turns out to be

$$E^{(3)}_{\mathrm{corr},S}=\sum_{i<j<k\epsilon S}\Delta\varepsilon_{ijk}\,, \tag{4}$$

with

$$\Delta\varepsilon_{ijk}=\varepsilon_{ijk}-\Delta\varepsilon_{ij}-\Delta\varepsilon_{ik}-\Delta\varepsilon_{jk}-\varepsilon_i-\varepsilon_j-\varepsilon_k\,, \tag{5}$$

and so on. The exact correlation energy of S is

$$E_{\mathrm{corr},S}=E^{(1)}_{\mathrm{corr},S}+E^{(2)}_{\mathrm{corr},S}+E^{(3)}_{\mathrm{corr},S}+\cdots\,. \tag{6}$$

The assumption that correlations between the different subsets of S are small ensures the rapid convergence with respect to the number of bodies. Still, each term in the incremental expansion of the correlation energy per unit cell involves an infinite sum with the sole exception of the one-body contribution.

Since electron correlations are a local effect in nonmetals, localized orbitals centered at different ions (or bonds in covalent crystals) are well suited as subsets for a rapidly converging series. Also, this justifies the use of finite clusters instead of the periodic solid to calculate the required matrix elements. Still, the transferability of individual increments from correlated cluster calculations to the crystal must be checked by calculating the increments in different chemical environments.

Concluding, one must ensure the convergence with respect to the number of centers and with respect to the distance between the centers. Last but not least, one must also guarantee the transferability of the increments between the different clusters and thereby from the clusters to the solid.

B. Computational details

Throughout this work we use energy-consistent scalar-relativistic *ab initio* pseudopotentials to reduce the computational effort and to incorporate the most important relativistic effects. The N^{5+} pseudopotential for nitrogen is the one proposed by Bergner *et al.*[23] (with $1s^2$ in the core). For gadolinium we use two sets of pseudopotentials, i.e., a Gd^{11+} pseudopotential and a Gd^{3+} pseudopotential. The Gd^{11+} pseudopotential employed in the CRYSTAL HF calculations and for the central finite cluster in the correlation calculations includes the $[\mathrm{Kr}]4d^{10}4f^7$ subconfiguration in the core. This leads to an atomic valence configuration of $5s^25p^66s^25d^1$ as derived by Dolg *et al.*[18] In order to model gadolinium atoms in the embedding region of the central clusters in correlation calculations, we additionally generated a Gd^{3+} pseudopotential with a $[\mathrm{Kr}]4d^{10}4f^75s^25p^6$ core.

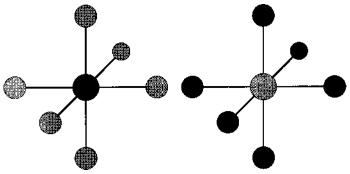

FIG. 1. Gd_6N cluster and GdN_6 cluster.

Corresponding primitive unpolarized Gaussian valence basis sets were generated using the atomic HF program ATMSCF.[24] The quality of the basis sets was verified by a comparison with numerical finite difference HF calculations for the atoms done with the program MCHF (Ref. 25) (representing the HF basis set limit). We also derived polarization/correlation functions and natural-orbital contractions in atomic calculations using the configuration interaction (CI) method with single and double excitations (CISD) with the molecular CI program MOLPRO.[20–22] Details will be given in the following two subsections.

1. Hartree-Fock calculation

Reliable HF calculations are a necessary precursor to the discussion of electron correlations in solids. We performed HF ground-state calculations for GdN using the program package CRYSTAL.[1] Our basis sets are a $(5s5p4d)/[4s4p2d]$ set for gadolinium and a $(5s5p1d)/[3s3p1d]$ set for nitrogen. Unfortunately, f functions are at present not implemented in the code. In order to account for polarization of the Gd-N bond a single s function has been placed at the middle of each bond, and optimized for the solid. Another problem of the computer code are convergence difficulties when diffuse exponents are included. For the atomic basis sets causing a divergence with CRYSTAL, we simply fixed the outermost exponent to the smallest possible value and reoptimized the remaining exponents. For Gd, s, p, and d, the smallest possible exponent was 0.11, whereas for nitrogen no fixing was necessary. Its outermost exponents were 0.1806 and 0.1852 for s and p, respectively. We optimized the nitrogen d exponent in CRYSTAL HF calculations for the solid (0.9).

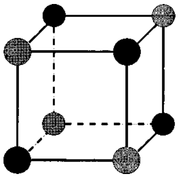

FIG. 2. Gd_4N_4 cluster.

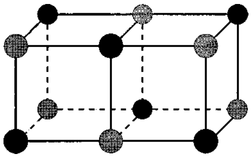

FIG. 3. Gd_6N_6 cluster.

2. Correlation calculation

Since electron correlations are mainly a local effect, the correlation-energy increments should not depend very much on the surroundings. We use this property to derive the increments from finite-cluster calculations. The various clusters considered are shown in Figs. 1–5. In each case, only the explicitly treated ions of the central clusters, modeled with Gd^{11+} pseudopotentials and N^{5+} pseudopotentials, are depicted. These central clusters are surrounded by one layer of Gd^{3+} pseudopotentials and point charges -3 at the nitrogen sites. The use of Gd^{3+} pseudopotentials to model the environment of explicitly treated nitrogen sites prevents the electrons of the latter ions from artificially collapsing toward the positive charge of the former ones. Each cluster and its first surrounding layer are embedded in at least four layers of point charges ± 3. Only for the octahedral clusters (see Fig. 1), we had to fit an array of point charges to correctly reproduce the Madelung potential, because these clusters are not electrically neutral.

To allow a small electron transfer from the central cluster to the environment, a single s contraction has been placed at the site of every Gd^{3+} pseudopotential. The basis sets were generated using the atomic HF program ATMSCF (Ref. 24) with diffuse/polarization functions optimized in atomic calculations at the CISD level. The uncontracted basis sets are $(7s6p5d3f2g)$ for gadolinium and $(6s6p3d2f)$ for nitrogen. The exponents of nitrogen d and f functions were taken from Dunning and co-workers augmented polarized correlation consistent valence triple ζ basis[26,27] set.

The contraction of these basis sets was obtained from the atomic natural orbitals at the CISD level in the same way as described in Ref. 28. This generalized contraction scheme was used to reduce the size of the basis sets while still retaining a reasonable accuracy. Following this construction we are lead to three different basis sets—A, B, and C, ordered in decreasing size. Every set is contained in the larger sets. The contractions are $[4s4p3d2f1g]$ for Gd and $[3s3p2d1f]$ for N (basis set A), $[3s3p2d1f]$ for Gd and $[2s2p1d]$ for N (basis set B), and $[3s2p2d1f]$ for Gd and $[2s2p1d]$ for N (basis set C). For nitrogen the contractions B and C are identical. With the exception of the octahedral clusters (see Fig. 1), in which we also calculated the one-site increment of the central ion with basis set A and its neighbors with basis set B, we used one type of basis set for all the atoms in a cluster (given in Table I).

We localized the canonical HF orbitals according to the Foster-Boys scheme. The correlation calculations were done at the coupled-cluster level with single and double excitations (CCSD) with basis set B/C, and for the one-site increments, also with basis set A. For testing purposes and to estimate the change to the better basis set A and to a better correlation treatment, we also calculated the one-site increments and the Gd-N two-site increment at the coupled-cluster level with single and double excitations augmented by a fourth-order perturbative estimate of the contribution of connected triple excitations $[\mathrm{CCSD}(T)]$ with basis sets A and B for an embedded GdN primitive cell. For the correlation calculations themselves, the test increments were not used because of the bad transferability from such a small cluster to the solid.

FIG. 4. Gd_4N_4 chain.

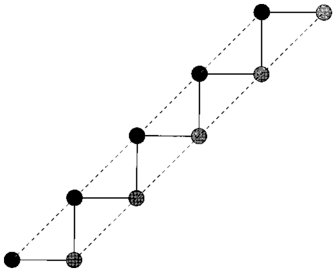

FIG. 5. Gd_5N_5 double chain.

III. RESULTS AND DISCUSSION

In this section, we will first comment on the accuracy of the present approach via test calculations and estimates. This will be followed by a comparison of our results with experimental values and other theoretical approaches.

A. Accuracy of the present approach

In the first subsection, we will discuss the errors in our HF treatment. The second subsection deals with errors and estimates at the correlated level.

1. Test of the Hartree-Fock treatment

Because we chose very stringent criteria for the integral tolerances and convergence parameters of the CRYSTAL program, the only type of error remaining at the HF level can be connected to basis set errors. As mentioned before, the CRYSTAL basis set lacks diffuse functions when applied to the separated atoms. In case of GdN, that is especially obvious for the Gd atom in its $4f^7 5d^1 6s^2\ {}^9D$ ground state (see Table II), where the insufficient basis set leads to a bad description of the diffuse $6s$ orbital and to an atomic energy 3.1 eV above the HF limit. The corresponding error of 0.1 eV for N in the $2s^2 2p^3\ {}^4S$ ground state is almost negligible. However, it is often claimed that in a solid the basis functions at other centers will take over the role of diffuse functions at a given center. Consequently a large basis set superposition error will lead to a too large cohesive energy if it is evaluated with respect to the atoms in the bare atomic CRYSTAL basis sets, i.e., we obtain 10.77 eV as an upper limit to the HF cohesive energy. Taking the HF limit for the energies of the free atoms yields a lower limit of 7.56 eV. In order to estimate the correct atomic energy of Gd and N, we performed a sequence of test calculations for the atoms (see Table II). Adding to the basis set of the central atom the nearest-neighbor basis sets as well as the bond-midpoint functions results in an upper limit of the cohesive energy of 9.52 eV. Adding

TABLE I. Correlation energy increments in a.u. determined at the CCSD level for a Gd-N bond length of $a/2=2.5$ Å; all distances are given in units of $a/2$; the distances for the three-site increments are ordered according to the rule: $1\text{-}2\text{-}3 \rightarrow r_{12}, r_{23}, r_{31}$.

Type	Cluster	Weight factor	Distance	Increment	Basis set
		One-site increments			
Gd	GdN_6	1	—	−0.116 262	*B*
N	$\mathrm{Gd}_6\mathrm{N}$	1	—	−0.214 382	*B*
		Two-site increments			
Gd-N	$\mathrm{Gd}_4\mathrm{N}_4$	6	1	−0.009 416	*B*
	$\mathrm{Gd}_4\mathrm{N}_4$	8	$\sqrt{3}$	−0.000 321	*B*
	$\mathrm{Gd}_6\mathrm{N}_6$	24	$\sqrt{5}$	−0.000 103	*B*
	$\mathrm{Gd}_4\mathrm{N}_4$ Chain	30	3	−0.000 035	*C*
N-N	$\mathrm{Gd}_4\mathrm{N}_4$	6	$\sqrt{2}$	−0.003 875	*B*
	GdN_6	3	2	−0.001 101	*B*
	$\mathrm{Gd}_6\mathrm{N}_6$	12	$\sqrt{6}$	−0.000 149	*C*
	$\mathrm{Gd}_5\mathrm{N}_5$ double chain	6	$2\sqrt{2}$	−0.000 049	*C*
Gd-Gd	$\mathrm{Gd}_4\mathrm{N}_4$	6	$\sqrt{2}$	−0.000 389	*B*
	$\mathrm{Gd}_6\mathrm{N}$	3	2	−0.000 094	*B*
		Three-site increments			
N-N-N	$\mathrm{Gd}_4\mathrm{N}_4$	8	$\sqrt{2}, \sqrt{2}, \sqrt{2}$	0.000 153	*B*
	GdN_6	12	$\sqrt{2}, \sqrt{2}, 2$	0.000 105	*B*
	$\mathrm{Gd}_6\mathrm{N}_6$	24	$\sqrt{2}, 2, \sqrt{6}$	0.000 007	*C*
N-N-Gd	$\mathrm{Gd}_4\mathrm{N}_4$	12	$\sqrt{2}, 1, 1$	0.000 222	*B*
	$\mathrm{Gd}_4\mathrm{N}_4$	24	$\sqrt{2}, 1, \sqrt{3}$	0.000 028	*B*
N-Gd-Gd	$\mathrm{Gd}_4\mathrm{N}_4$	12	$1, \sqrt{2}, 1$	0.000 043	*B*
Gd-Gd-Gd	$\mathrm{Gd}_4\mathrm{N}_4$	8	$\sqrt{2}, \sqrt{2}, \sqrt{2}$	0.000 005	*B*

furthermore the most important diffuse basis functions on the next-nearest- and third-nearest-neighbor sites, i.e., placing the atom of interest with the full basis set in the center of a 3^3 cluster and providing the most important basis functions on all 3^3-1 surrounding dummy sites, yields 7.86 eV as an upper limit to the HF cohesive energy. Alternatively, augmenting the CRYSTAL basis set by diffuse functions for the atomic calculations, we obtain 7.78 eV as an estimate for the actual HF cohesive energy, i.e., a value in good accord with the lower and upper bounds of 7.56 and 7.86 eV, respec-

TABLE II. Ground-state energies of the free atoms in a.u. (atomic units) with different basis sets at different theoretical levels.

Basis	Atom	HF	CCSD	CCSD(*T*)
Numerical finite difference	Gd	−35.386 406		
	N	−9.667 649		
CRYSTAL	Gd	−35.272 303		
	N	−9.663 838		
+nearest-neighbor basis sets	Gd	−35.317 580		
	N	−9.664 563		
$+3^3-1$ neighbors	Gd	−35.378 309		
	N	−9.664 641		
CRYSTAL+diff. functions	Gd	−35.381 390		
	N	−9.664 513		
A	Gd	−35.381 253	−35.663 663	−35.675 911
	N	−9.663 998	−9.784 041	−9.786 708
B	Gd	−35.381 124	−35.569 684	−35.576 586
	N	−9.663 845	−9.767 470	−9.768 334

TABLE III. Correlation energy increments in a.u. at the CCSD and CCSD(T) levels with different basis sets for a Gd-N bond length of $a/2=2.5$ Å evaluated for an embedded GdN primitive cell.

Increment	Basis B		Basis A	
	CCSD	CCSD(T)	CCSD	CCSD(T)
Gd	−0.116 369	−0.117 971	−0.195 058	−0.199 372
N	−0.189 730	−0.193 133	−0.240 720	−0.249 023
Gd-N	−0.009 896	−0.010 987	−0.013 575	−0.015 374

tively. This indicates that the correct cohesive energy is closer to the value following the counter-poise method (7.86 eV).

2. Test of the correlation treatment

The approximations at the correlated level mainly fall into two classes, i.e., the incompleteness of the one-, and, partly as a consequence, the many-particle basis set, and the cutoffs used in evaluation of the incremental expansion. At the correlated level we can estimate the error arising from the incompleteness of the one-particle basis set. We obtain this estimate from the embedded GdN primitive cell. There we computed the ratio between the two-site Gd-N increments obtained with the basis sets A and B. This ratio amounts to 1.37 (see Table III). We then multiplied by 1.37 the two- and three-site increments obtained with basis set B in order to obtain the estimate for these increments with basis set A. The one-site increments were calculated with both basis sets in the octahedral clusters. As a result, the improvement of the basis set from B to A is expected to account for an increase of 1.17 eV (9.4%) of the cohesive energy and a concomitant decrease of 0.035 Å (0.7%) of the lattice constant (see Table IV). The reason to scale the two- and three-site increments in addition to actually calculating the one-site increments with basis set A is that the one-site increments tend to increase the lattice constant in contrast to the two- and three-site increments. This can be seen in Table V. Therefore, it would introduce a systematic error if these groups of increments are treated with different one-particle basis sets. Last but not least, the basis set superposition error amounted to 0.52 and 0.09 eV for basis sets B and A, respectively, and was corrected by the counter-poise method.[29]

With respect to the many-electron basis set, the inclusion of triples in the coupled-cluster expansion leads to an increase of approximately 0.37 eV (3.0%) in the cohesive energy for basis set A, and 0.2 eV (1.6%) for basis set B. These numbers were estimated by calculating the one-site increments at the CCSD(T) level in the octahedral clusters, and scaling the other increments by a common factor which only depends on the basis set. This factor (1.133 for basis set A and 1.110 for basis set B) was obtained for the Gd-N two-site increment calculated in the embedded GdN primitive cell at the CCSD and CCSD(T) levels in a similar way as for the one-particle basis set scaling (see Table III). Higher-order contributions are expected to be significantly smaller.

Now we will comment on the cutoff of the incremental series. We chose an energetic cutoff, i.e., we neglected every increment that contributed less than 0.03 eV, to the correlation energy, including its weight factor for a bond length of 2.5 Å. In Table I the fast convergence with respect to the number of centers as well as to the distance between the centers can be seen. As a consequence, the error with respect to the cutoff should be of the order of 0.1 eV.

Finally, the transferability of the increments between the different clusters has to be studied. As examples, we discuss the nitrogen one-site increment and the Gd-N nearest-neighbor two-site increment (both quantities evaluated using basis B and the almost identical basis C). The nitrogen one-site increment varies between −5.168 eV in the octahedral cluster with Gd in the middle (see Fig. 1), and −5.834 eV in the octahedral cluster with N in the middle (see Fig. 2) whereas the Gd-N nearest-neighbor two-site increment varies between −0.223 eV in the single chain (see Fig. 4) and −0.269 eV in the double chain (see Fig. 5). Of course, the basis sets are slightly different because of the different surrounding basis sets—the nitrogen has in the first case (smallest value) only one Gd nearest-neighbor basis set, whereas in the second case it is surrounded by six Gd basis sets. We have always taken the increments from the best possible em-

TABLE IV. Results for the cohesive energy in eV, the lattice constant in Å, and the bulk modulus in GPa, the comparison with experiment is given in %.

	Cohesive energy	Lattice constant	Bulk modulus
Hartree-Fock	7.865 (63.4%)	5.114 (102.6%)	130.6
Incremental expansion (CCSD)			
Basis B/C	10.67 (86.0%)	5.084 (102.0%)	140.3
Basis A estimate	11.84 (95.5%)	5.049 (101.3%)	163.8
Incremental expansion [CCSD(T)]			
Basis B/C estimate	10.87 (87.7%)		
Basis A estimate	12.21 (98.5%)		
Experiment (Refs. 30–34)	12.40±0.26 (100%)	4.986 (100.0%)	192±35
LSDA (Refs. 19 and 37)			
paramagnetic state	11.75 (94.8%)	4.977 (99.8%)	188.5
ferromagnetic state	11.91 (96.0%)	4.977 (99.8%)	188.5

TABLE V. Energy contributions in a.u. as functions of the lattice constant *a* in Å; the basis sets used are given in parentheses; ex: extrapolated; es: estimated.

a	4.90	4.95	5.00	5.05	5.10	5.15
E_{HF} (CRYSTAL)	$-45.311\,111^{\mathrm{ex}}$	$-45.324\,394^{\mathrm{ex}}$	−45.329 058	−45.331 167	−45.331 933	−45.331 762
One site (*B*)	−0.328 115	−0.329 376	−0.330 644	−0.331 920	−0.333 203	−0.334 491
Two Site (*B*/*C*)	−0.096 849	−0.094 497	−0.092 303	−0.090 189	−0.088 208	−0.086 324
Three Site (*B*)	0.005 396	0.005 272	0.005 148	0.005 092	0.004 968	0.004 888
One site (*A*)	−0.434 638	−0.435 973	−0.437 282	−0.438 578	−0.439 851	−0.441 106
Two Site$^{\mathrm{es}}$ (*A*)	−0.132 683	−0.129 461	−0.126 455	−0.123 559	−0.120 845	−0.118 264
Three Site$^{\mathrm{es}}$ (*A*)	0.007 393	0.007 223	0.007 053	0.006 976	0.006 806	0.006 697
E_{corr} (*B*/*C*)	−0.419 568	−0.418 601	−0.417 799	−0.417 017	−0.416 443	−0.415 927
$E^{\mathrm{es}}_{\mathrm{corr}}$ (*A*)	−0.559 928	−0.558 211	−0.556 684	−0.555 161	−0.553 890	−0.552 673
E_{Total} (*B*/*C*)	$-45.730\,679^{\mathrm{ex}}$	$-45.742\,995^{\mathrm{ex}}$	−45.746 857	−45.748 184	−45.748 376	−45.747 689
$E^{\mathrm{es}}_{\mathrm{Total}}$ (*A*)	$-45.871\,039^{\mathrm{ex}}$	$-45.882\,605^{\mathrm{ex}}$	−45.885 742	−45.886 328	−45.885 823	−45.884 435

bedding. Overall, we expect the transferability error between our cluster calculations and the periodic system to be of the order of a few tenths of an eV.

B. Results and comparison with experiment

In order to optimize the geometry at the correlated level, we calculated the total energy for six different lattice constants (see Table V). Our final results are compared to experimental data in Table IV. In this table, one can also see the changes in the one- and many-electron basis sets. We obtained a lattice constant of 5.114 Å (+2.6% larger than the experimental result) at the HF level and 5.084 Å (+2.0%) at the CCSD level, with basis set *B*/*C* in reasonable agreement with the experimental value [4.986 Å (Refs. 30–33)]. The estimate for basis set *A* at the CCSD level leads to 5.049 Å(+1.3%). In addition, we calculated a bulk modulus of 140.3 GPa with basis set *B*/*C*, and estimated 163.8 GPa with basis set *A* (the HF result amounts to 130.6 GPa). Almost all the values are in agreement with the experimental bulk modulus[34] of 192±35 GPa because of its large error bar. Therefore we do not provide the comparisons in percent. The experimental heat of decomposition at 298 K of GdN into Gd_g and N_2 [174±6 kcal/mol (Ref. 23)] was extrapolated to 0 K using the experimental specific heat[30] and corrected for zero-point vibration using the Debye model [$\Theta_D \approx 400$ K (Ref. 30)]. To that, the experimental dissociation energy of N_2 (Ref. 35) was added to give the experimental cohesive energy of 12.40±0.26 eV per unit cell. The computed cohesive energy, i.e., the total energy per unit cell for the solid minus the sum of the total energies of the free atoms, accounts for 63.4% (7.865 eV) of the experimental cohesive energy at the HF level, increasing to 86.0% (10.67 eV) including electron correlations with basis set *B* at the CCSD level, and again increasing to 95.5% (11.84 eV) for the basis set *A* estimate at the CCSD level. The triples correction finally leads to 87.7% (10.87 eV) of the experimental cohesive energy with basis set *B*/*C* and 98.5% (12.21 eV) for the basis set *A* estimate. Taking into account the errors which were summarized in Sec. III A, we attained excellent, albeit in the last case slightly fortituous, agreement with experiment.

Summing up, improving the one-particle basis set increases the cohesive energy, reduces the lattice constant, and increases the bulk modulus. Additionally, augmenting the coupled-cluster expansion increases the computed cohesive energy even more.

Finally, a comment on the ionicity of GdN appears to be in order. A qualitative measure of this ionicity are the Mulliken charges from CRYSTAL (Ref. 1) HF calculations assigned to the pseudopotential centers: 9.05 for Gd($\approx +2$ valence) and 6.94 for *N* (≈ -2 valence). Of course, for a quantitative analysis of the ionicity of GdN, Mulliken's analysis is inappropriate because of its strong basis set dependence. However, we merely want to point out that GdN is considerably less ionic than the metal oxides MgO, CaO, and NiO, to which the incremental method has been applied previously.[13–15] Therefore, computationally more demanding cluster models had to be applied.

C. Comparison to related calculations

In this subsection we briefly comment on work of others.[19,36,37] To our knowledge, the first *ab initio* calculations were the band-structure calculations of Hasegawa and Yanase.[36] However, these authors did not optimize the geometry and also did not compute the cohesive energy. The most recent calculations were done by Pethukov, Lambrecht, and Segall,[19,37] who reached a very good agreement with experiment using a density-functional approach. They calculated cohesive properties both for the ferromagnetic and the paramagnetic ground state within the local spin density approximation (LSDA). Similar to us they treated the $4f$ electrons as atomic with a fixed occupancy. Their lattice constant amounted to 4.977 Å, only 0.2% below the experimental value. For the cohesive energy they obtained 11.75 eV for the paramagnetic phase and 11.91 eV for the ferromagnetic phase (94.8% and 96.0% of the experimental value). In addition, they computed a bulk modulus of 188.47 GPa.

These numbers are in excellent agreement with experimental data as well as our estimated results. However, our calculated values with basis set *B*/*C* are not as close to experiment as theirs. It seems that the functional approximation which is not required in our approach is a very good approximation for GdN. If we compare the result for basis set *B*/*C* with the estimate for basis set *A* in our approach, the basis set defect can be seen. On the other hand, increased computer power and further program development will make actual calculations feasible, where at present only estimates are possible.

IV. CONCLUSION

In conclusion, we have shown that the incremental scheme using quantum-chemical methods is capable of accurately treating compounds containing rare-earth elements of a fixed valency. We obtained (estimated) approximately 86.0% (98.5%) of the cohesive energy for the model system GdN. Our calculated (estimated) value for the lattice constant overshoots the experimental lattice constant by 2.0% (1.3%). We calculate (estimate) a bulk modulus of 140.3 GPa (163.8 GPa), which is still considerably lower than the density-functional result of Ref. 19. Although much more cost efficient and still attaining very good results, density-functional theory is not improvable in a straightforward way, in contrast to our present wave-function-based approach. This is, to our opinion, and confirmed by the estimates of Sec. III, an advantage of our method. Also, it seems to us easier to interpret the results and analyze individual contributions. Work is underway in our laboratory to explicitly calculate the interaction between the f electrons on different gadolinium atoms in GdN.

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