Crystal structure and phase stability of Co$_2$N: A combined first-principles and experimental study

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**Abstract**

The crystal structure and phase stability of Co$_2$N are revisited based on experiments and first-principles calculations. Powder X-ray diffraction (PXRD) measurements and Rietveld refinements clearly confirm that the stable crystal structure of Co$_2$N is an isotype of $\eta$-Fe$_2$C and Co$_2$C with the space group $Pnmm$ rather than the closely related $\zeta$-Fe$_2$N with the space group $Pbcn$. The refined lattice parameters of Co$_2$N in the $Pnmm$ structure are $a = 4.6108(1)$ Å, $b = 4.3498(1)$ Å, $c = 2.85592(7)$ Å, obtained from X-ray diffraction using synchrotron radiation. Furthermore, differential scanning calorimetry (DSC) with subsequent diffraction experiments reveal an endothermal transition to an $\epsilon$-type order at 398 °C followed by an exothermal decomposition at 446 °C. First-principles density-functional-theory (DFT) calculations including the Hubbard $U$ correction (DFT+$U$) demonstrate that it is essential for transition metal nitrides to consider strong electron correlation to predict the correct experimental structure and magnetic state. In particular, an effective value of $U_{\text{eff}} = 2.75$ eV can be utilized to obtain an antiferromagnetic $Pnmm$ phase of Co$_2$N in agreement with experiments.

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1. Introduction

3d transition metal nitrides are an interesting and long-standing topic for science and industry because of their unique properties such as hardness and corrosion resistance [1]. Yet, their synthesis remains challenging. Direct nitriding reactions between a metal and nitrogen at ambient pressure often do not lead to the desired nitride, particularly for highly nitrided phases and for the late transition metal nitrides in general, due to thermodynamic reasons [1,2]. As regards the cobalt nitrides, the first successful synthesis dates back to 1901 [3] when the formation of a cobalt nitride with the composition of Co$_4$N$_2$ ($\equiv$ Co$_2$N) was proposed. Until now four cobalt nitrides have been established, namely CoN (three possible modifications: sphalerite-, rock-salt-, and NiAs-type [2,4–7]), Co$_2$N [8], Co$_3$N [8], and Co$_4$N [9]. Additionally, during laser-heating in nitrogen at high pressures a marcasite-type pernitride with a composition of Co$_3$N$_2$ was obtained [7]. Besides the binary phases, ternary cobalt nitrides such as Co$_2$Mo$_3$N [10], Co$_3$Mo$_3$N [10], and Li$_3$Co$_2$N [11] are known.

For the production of Co$_2$N, which is in our focus, there are several possibilities: Juza and Sachsze [8] reported the ammonolysis of different starting materials, which partially had to be reduced in H$_2$-flow in an initial step prior to the nitridation in ammonia. The direct reaction between Co and N$_2$ requires high-pressure high-temperature conditions (supercritical nitrogen fluid at 1527 °C and about 10 GPa using a diamond anvil cell and YAG laser heating) to form Co$_2$N [2]. Another reported synthetic route uses a supercritical ammonia-methanol mixture between 170 °C and 290 °C at about 16 MPa to achieve nanostructured particles of Co$_2$N [12]. Direct current reactive sputtering deposition was applied to obtain thin films of Co$_2$N in a mixture with other cobalt nitrides [13]. Recently, we have obtained rather well crystallized...
Co$_2$N samples of good purity from decomposition of the azide precursor [Co(NH$_3$)$_5$N$_3$]Cl$_2$ in flowing ammonia [14].

The crystal structure of Co$_2$N was already reported to be isotypic to the structure of the respective cobalt carbide (Co$_2$C) and iron carbide (Fe$_2$C) with the corresponding compositions [15,16], i.e., to the CaCl$_2$-type structure with the space group Pnnm. Information on structural data of Co$_2$N is, however, rather limited [2,15], contingent on its challenging synthesis. For example, during the formation of Co$_2$N, hexagonal Co$_2$N is a frequent by-product, difficult to avoid and also difficult to detect due to strongly overlapping reflections in the diffraction patterns [8,14]. A further challenging aspect is the structural similarity of the Pnnm structure to the α-PbO$_2$-type structure with space group Pbcn that is found for the chemically closely related iron nitride phase ζ-Fe$_2$N [17]. One can consider Pbcn Co$_2$N by replacing Fe in ζ-Fe$_2$N with Co and modification of lattice parameters. The thus obtained Pbcn Co$_2$N is topologically similar to the Pnnm Co$_2$N as emphasized in Fig. 1. In both structures, the Co atoms form the motif of a hexagonal close-packing (hcp) distorted into an orthorhombic structure. Within this hcp of Co, N atoms occupy half of the octahedral voids [8,14].

![Fig. 1. Schematic representation of Co$_2$N in the Pnnm and Pbcn structures from the direction perpendicular to the close-packed Co layers. Dark and light gray spheres represent Co atoms in the A and B layers, respectively. Blue and orange octahedra show the N sites in the c1 and the c2 layers, respectively. Orientation relations between the ideal hcp Co lattice and Co$_2$N are also shown. Visualization was performed using VESTA [23]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image1)

![Fig. 2. Schematic representation of the collinear AFM states considered in the present first-principles calculations. Dark and light gray spheres represent the Co atoms in the A and the B layers, respectively. Small white spheres show the N sites in the c1 and the c2 layers, half of which are occupied in a different manner depending on the crystal structure as shown in Fig. 1. Blue and orange arrows on the Co atoms represent the spin-up and the spin-down magnetic moments, respectively. Orientation relations between the ideal hcp Co lattice and Co$_2$N (both in the Pnnm and the Pbcn structures) are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image2)
edges and corners. The only difference between the two structures is the N ordering. Namely, in the Pnnm structure N atoms are arranged in straight corridors in each of the c1 and the c2 layers, while in the Pbcn structure N atoms feature a zigzag arrangement. A conclusive structure identifi
cation needs to take this structural similarity between Pnnm and Pbcn carefully into account, and this is one goal of the present study.

First-principles calculations are nowadays very common for transition metal oxides, carbides, as well as nitrides. For transition metal oxides, the importance of strong electron correlation is well accepted, and it is essential to consider the proper methodology, such as density-functional-theory (DFT) including the Hubbard $U$ correction, i.e., DFT+$U$ [18]. For transition metal carbides and nitrides, in contrast, research on the impact of strong electron correlation is rather limited, although its importance has been reported [19–21]. A good example is given by CrN for which pure DFT wrongly predicts a nonmagnetic (NM) phase to be the most stable [21]. Only when considering the strong electron correlation, the experimentally observed antiferromagnetically (AFM) ordered orthorhombic phase [22] can be correctly stabilized [21]. For Co$_2$N, detailed investigations on the impact of strong electron correlation have not been reported yet, and this is the second goal of the present study.

Thus, in this paper, the phase stability and the structural parameters of Co$_2$N are revisited based on both experiments and first-principles calculations. Improved structural parameters are derived by performing powder X-ray diffraction (PXRD) measurements with synchrotron radiation. Rietveld refinements allow us to substantiate that the crystal structure of Co$_2$N has Pnnm symmetry. Decomposition of Co$_2$N at elevated temperatures is also studied using
Table 1
Detailed data of Rietveld refinements for the synchrotron-radiation PXRD (Fig. 3(a)) obtained in the present study. Source: synchrotron (ID22, ESRF, Grenoble, France). Temperature: 295 K. Pressure: 101.325 kPa. Wavelength: 0.335914(5) Å. Obtained in the present study. Source: synchrotron (ID22, ESRF, Grenoble, France).

Table 2
Comparison of structural parameters of Co$_2$N, Co$_3$N, and fcc Co obtained from Rietveld refinements for the present synchrotron-radiation PXRD data with those from previous experimental studies. In fcc Co$_3$N, Co and N atoms are located at the Wyckoff sites of 4(g) (x, y, 0) and 2(a) (0, 0, 0), respectively. In hexagonal $P6_3\overline{2}2_1$ Co$_3$N, Co atoms are located at 6g (x, 0, 0) while N atoms are located at 2c (1/3, 2/3, 1/4) and at 2b (0.0, 0.1, 0.1). In fcc $Fm\overline{3}m$ Co, Co atoms are located at the Wyckoff site of 4a (0, 0, 0). The values obtained from the present DFT+U calculations for the AFM $Pmmn$ phase with $U_{eff} = 2.75$ eV are also displayed.

2. Experimental details

2.1. Synthesis

All manipulations for the synthesis of Co$_2$N were carried out in an argon filled glovebox (MBraun, p(O$_2$) < 0.1 ppm). Metastable Co$_2$N was synthesized by ammonolysis of [Co(NH$_3$)$_2$N$_3$]Cl$_2$. A modified reaction protocol based on the one reported in literature [14] was used: (i) 350 °C (8 h) or (ii) 450 °C (12 h) followed by cooling to 350 °C within 12 h. In all cases an ammonia flow (> 99.999 %) of 60 ml/min was applied. The precursor [Co(NH$_3$)$_2$N$_3$]Cl$_2$ was synthesized according to Linhard and Flygare [24]; CoCl$_2$·6H$_2$O was dissolved in a small amount of deionized water and mixed with an aqueous solution of NaN$_3$, NH$_4$Cl, and NH$_3$. This mixture was stirred at 60 °C for 2 h. After that the reaction mixture was cooled down in an ice bath for a complete precipitation. The obtained precipitate was washed with diluted hydrochloric acid and ethanol several times. To further purify the precursor by recrystallization, it was dissolved in deionized water and precipitated by a careful addition of concentrated hydrochloric acid. After washing with ethanol the product was dried at 50 °C for several days.

2.2. Characterization

PXRD measurements were carried out at ambient temperature in the following two conditions:

- At the ID22 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France ($\lambda = 0.335914(5)$ Å) using a 9-element detector array (high resolution setup). The data collection was performed in a 2θ range of 5–35° in transmission geometry. The sample of Co$_2$N was located in a 0.7 mm diameter Kapton® capillary and installed parallel to the axis of the diffractometer. This was performed for Rietveld refinements of the structure of Co$_2$N.
- On a STOE Stadi-P diffractometer equipped with a Ge(111) monochromator and a Mythen 1K detector using Mo-K$_{\alpha 1}$ radiation. The data collection was performed in a 2θ range of 5–65° in transmission geometry. This measurement was performed in order to check the sample quality prior to the measurements at the synchrotron source and to investigate the existing phases after the DSC experiments.

Rietveld refinements of Co$_2$N were carried out using the FullProf program suite [25].

DSC experiments were performed on a DSC204F1 Phoenix (Netzsch Gerätebau GmbH) in cold-welded aluminium pans using a heating rate of 10 K/min in flowing argon atmosphere.
3. Computational details

For the DFT calculations, we modeled CoN in Pnmm and Pbcn symmetry using unit cells with 6 and 12 atoms, respectively. In the Pnmm structure, Co and N occupy the 4g and the 2a Wyckoff positions, respectively. In the Pbcn structure, Co and N occupy the 8d and the 4c Wyckoff positions, respectively. We employed the projector augmented wave method [26] and the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) form [27] implemented in the VASP code [28,29] in combination with the provided potentials [30]. The 3d4s and the 2s2p orbitals of Co and N, respectively, were treated as valence states. The plane-wave cutoff was set to 550 eV. Γ-centered 12×12×20 and 12×10×12 k-point meshes were applied for the Pnmm and the Pbcn structures, respectively, and the Methfessel-Paxton scheme [31] was employed with a smearing width of 0.1 eV. Total energies were minimized until they were converged to within 10⁻⁵ eV per unit cell. Cell volume, cell shape, and internal atomic positions were optimized so that the forces on atoms and the stress components on the unit cells are less than 2×10⁻⁴ eV Å⁻¹ and 2×10⁻⁵ eV Å⁻³, respectively. Strong on-site electron correlation was considered employing the rotationally invariant DFT+U formalism of Dudarev et al. [32], with Ueff = U − J varied in a range of 0–4 eV. Volumes, charges, and magnetic moments on Co and N atoms were computed based on the Bader analysis [33] employing the Yu-Trinkle algorithm [34] as implemented by Henkelman et al. [35–37].

In a previous experimental study [14], Co2N was found to be in an AFM state at very low temperatures with a Néel temperature of 10 K. To investigate the impact of magnetic ordering on the phase stability of Co2N, in the present first-principles calculations, we conducted collinear spin-polarized calculations of several model AFM states (Fig. 2) as well as of the ferromagnetic (FM) and the NM states. The formation energy per atom, ΔEₗ, of Co2N was computed as

\[
\Delta E_l = \frac{1}{3} \left( \frac{E(Co)}{(Co_2N)} - \left[ 2E(Co) + \frac{1}{2}E(N_2) \right] \right),
\]

where E(Co₂N) is the energy of Co₂N per formula unit. The energy of pure FM hcp Co, E(Co), was computed by optimizing the cell volume and the cell shape for the same Uₚ as that used for Co₂N. A 22×22×14 k-point mesh was used to sample the Brillouin zone of the two-atom Co hcp cell. The energy of a nitrogen molecule, E(N₂), was computed with spin-polarization and by optimizing the bond distance. To minimize the interaction with periodic images, a large unit cell of 20 Å × 20 Å × 20 Å and the Γ-point for sampling the Brillouin zone were used.

4. Results and discussion

4.1. Rietveld refinements

Due to its metastable nature, the synthesis of bulk Co₂N in high purity remains rather difficult. Further optimization of the annealing route of the [Co(NH₃)₃N₁₂]Cl₂ precursor [14,24] by variation of decomposition and annealing temperature, cooling rate, and flow conditions of ammonia finally reproducibly led to samples, which contained only small admixtures of Co₂N (strictly, Co₂N₁₋ₓ with x = 0.14(5)) and face-centered cubic (fcc) Co. Due to severe reflection overlap, these impurity phases are only noticeable on close inspection of the PXRD patterns and reveal as shoulders of reflections belonging to the title phase or by small intensity deviations from expected values. The graphical representation of the Rietveld refinements of the X-ray diffraction data is presented in Fig. 3(a), and further details of the Rietveld refinements are summarized in Table 1. The dominant phase is represented by Co₂N with 83(1) wt.%, followed by the impurity phases of Co₃N (12(1) wt.%) and CoN (5(1) wt.%) with...
fcc Co (5(1) wt.%). In Table 2 the observed lattice parameters of both nitride phases and fcc Co are compared with earlier reported data and confirm good agreement. Deviations may be due to slight variations in nitrogen content of the different phases studied, as such interstitial transition metal nitrides are generally prone to show homogeneity ranges [1]. A composition of Co$_3$N$_{1.14}$ was determined for the nitride impurity phase, which is in reasonable agreement with the previously reported value of Co$_3$N$_{1.1}$ determined by thermogravimetric analysis [14]. Fcc Co represents the high temperature phase of cobalt stable above about 420 °C [39] but may be readily quenched to room temperature [38]. For comparison, Rietveld refinements of the crystal structure of Co$_2$Ni in Pbcn, i.e., in the ζ-Fe$_2$N-type structure, are presented in Fig. 3(b). While at a first glance a similar Rietveld pattern to that for the Pnnm structure is obtained (because of the similarity of the Pnnm and the Pbcn structures as described in Fig. 1), a closer inspection reveals that e.g. the reflections measured at $2\theta = 6.07^\circ$ and $2\theta = 9.77^\circ$ are not reproduced. These reflections formally correspond to 101$_{Pbcn}$ and 201$_{Pbcn}$, respectively, but are forbidden for Pbcn according to the reflection condition of $l = 2n$ for h0l related to c-gliding [40]. The refinements with the Pbcn structure, furthermore, misproduce the 110$_{Pbcn}$ and the 112$_{Pbcn}$ reflections at $2\theta = 5.55^\circ$ and $2\theta = 10.02^\circ$, respectively, which are not observed in the measured PXRD data. It is thus clearly demonstrated that Co$_2$N crystallizes in the Pnnm structure rather than in the Pbcn structure.

4.2. Differential scanning calorimetry (DSC)

Fig. 4 shows the DSC measurement of Co$_2$N between 20 °C and 550 °C with a heating rate of 10 K/min in an argon atmosphere. At an onset temperature of 398 °C there is a small endothermal signal with an enthalpy of +1.8 J/g followed by a stronger exothermal signal with an enthalpy of −200 J/g at an onset temperature of 466 °C. A sample heated to a slightly higher temperature than the occurrence of the endothermal signal contained two phases, namely Co$_2$N (67(1) wt.%) and Co$_3$N$_{1.34}$ (33(1) wt.%), according to PXRD using Mo-K$_\alpha$ radiation (Fig. 5 and Table 3). This indicates a significant increase of the fraction of the Co$_3$N phase. Rietveld refinements after the DSC measurement showed a slightly higher nitrogen content in Co$_3$N$_{1.34}$ ($x = 0.34(15)$) than that before the DSC measurement ($x = 0.14(5)$) via occupation of a further nominally empty octahedral void, as was earlier observed, although to a much smaller extent [14]. A similar increase in nitrogen content is found also in Mn–N [41] and Fe–N [42,43] systems during decomposition of the respective nitride phase. The resulting composition corresponds closely to a Co$_2$N phase (Co$_3$N$_{1.34}$ = Co$_2$N$_{0.90}$) with the

Fig. 6. Formation energies per atom $\Delta E_f$ of Co$_2$N as a function of $U_{\text{eff}}$ from the present DFT+$U$ calculations. The obtained ground state at each $U_{\text{eff}}$ is shown at the bottom. The experimental formation energy of Co$_2$N expected from the present DSC measurement is shown by the thin dotted horizontal black line.
\(\varepsilon\)-type order, as similarly known for \(\varepsilon\)-Fe\(_3\)N\(_{1+x}\) with \(x\) up to about 0.5, i.e. \(\varepsilon\)-Fe\(_3\)N\(_\text{NM}\) [44,45]. Earlier simultaneous differential thermal analysis and thermal gravimetric analysis (DTA/TG) measurements indicated a weight loss starting at around 370 °C with an exothermal signal at 429.6 °C for Co\(_2\)N, while Co\(_3\)N started to decompose at around 420 °C with an exothermal signal at 593 °C [14]. The exothermal decomposition in every case directly results in the formation of fcc Co.

4.3. First-principles calculations

Fig. 6 shows the formation energies of Co\(_2\)N obtained from the DFT+U calculations. For the whole investigated range of the effective Hubbard U value, i.e., \(U_{\text{eff}} = 0\)–4 eV, all considered phases show positive formation energies \(\Delta E_f\), in consistency with the metastability of Co\(_2\)N observed in experiments. However, for \(U_{\text{eff}} = 0\) eV (i.e., pure DFT), all magnetic states converge to the NM state for both the \(Pnmn\) and the \(Pbcn\) structures, which is inconsistent with the experimental finding of an AFM state [14]. The magnetic states are rapidly stabilized with respect to the NM state with increasing \(U_{\text{eff}}\). In particular, the AFM configurations are preferentially stabilized for \(U_{\text{eff}} \geq 1.5\) eV. This finding highlights the necessity to consider the strong on-site electron correlation to stabilize the AFM states in agreement with experiment. Yet, although the magnetic state is correctly predicted when utilizing a \(U_{\text{eff}}\) within 1.5–2.5 eV, the \(Pbcn\) phase is energetically more stable than \(Pnmn\), which is again inconsistent with our detailed experimental analysis provided above. In order to obtain not only the correct magnetic state but also the correct crystallographic structure, i.e., \(Pnmn\), as the energetically most stable one, the value of \(U_{\text{eff}}\) needs to be taken within the range of 2.5–3.5 eV. For a higher \(U_{\text{eff}}\) (up to the maximum investigated \(U_{\text{eff}}\) of 4 eV), again the experimentally excluded \(Pbcn\) phase is energetically more stable than the \(Pnmn\) phase.

Our calculations highlight that we can obtain simulation results that are consistent with the experimental phase stability and magnetic state only within a limited \(U_{\text{eff}}\) range of 2.5–3.5 eV. In particular, it is the AFM \(Pnmn\) Co\(_2\)N phase that is the most stable for these \(U_{\text{eff}}\) values. In fact for \(U_{\text{eff}} = 2.75\) eV, we can also obtain a very good agreement between the \(ab\text{ initio}\) formation energy, \(\Delta E_f\), and the exothermal phase transition observed from the present DSC measurements, 200 J/g \(\approx 91\) meV/atom. It is worth mentioning that the \(U_{\text{eff}}\) range of 2.5–3.5 eV includes the value reported to be suitable for cobalt oxides [18]; i.e., \(U_{\text{eff}}\) of 3.3 eV which was used to reproduce the experimental oxidation energies from CoO to Co\(_3\)O\(_4\) [18]. This \(U_{\text{eff}}\) value also reproduces the experimentally observed rock-salt-type structure of CoO\(_{0.75}\)N\(_{0.25}\) at the experimental volume [14]. Our present results further support that a \(U_{\text{eff}}\) in the 2.5–3.5 eV range should be a safe choice for cobalt nitrides as well as oxides.

For \(U_{\text{eff}} > 2\) eV, the AFM3 state is energetically more stable than any other considered magnetic state for both the \(Pnmn\) and the \(Pbcn\) structures. It should be emphasized that, without the AFM3 state, we would not obtain the \(Pnmn\) structure to be more stable than the \(Pbcn\) structure despite the inclusion of the strong on-site electron correlation via DFT+U. This reveals the importance of a careful consideration of various magnetic candidate states when investigating cobalt nitrides. Note that the true AFM ground state of
Co$_2$N might have noncollinear magnetic moments, the consideration of which is beyond the scope of the present study. Nevertheless, the here considered collinear AFM state explains well the experimental phase stability and hence can be used to model Co$_2$N in a rather straightforward manner. Our results thus provide guidance to future first-principles calculations.

Fig. 7 shows the structural parameters of Pnmm Co$_2$N obtained from the DFT+U calculations. For the unit cell parameters (Fig. 7(a)–7(c)), the values of the (unrealistic) NM state and of the magnetic states tend to underestimate and overestimate the experimental values, respectively. For the atomic coordinates (Fig. 7(d) and (e)), the situation is less transparent and depends strongly on the magnetic state. Note that there is no single $U_{\text{eff}}$ value for which we would observe good agreement for all structural parameters, neither for the “good” range of $U_{\text{eff}} = 2.5$–3.5 eV nor for the remaining investigated range up to $U_{\text{eff}} = 4$ eV. We attribute this to the well-known systematic deviation of DFT lattice parameters [46], which is very likely inherited by the present DFT+U calculations. It is, nevertheless, demonstrated that both the magnetic condition and the strong on-site electron correlation largely affect the structural parameters. For example, for $U_{\text{eff}} = 2.75$ eV which lies in the range for which we observe the correct structural and magnetic ground state, we find structural parameters as given in Table 2.

Fig. 8 shows the local atomic volumes, charges, and magnetic moments of Co$_2$N from the DFT+U calculations based on the Bader analysis [33]. Co shows a larger atomic volume than N. Magnetic states show larger volumes than the NM state both for Co and for N. It is also found that Co and N are charged positively and negatively, respectively, consistently with their electronegativities (in the definitions of Pauling [47] and Allen [48–50]). Further, the charges are not strongly dependent on the magnetic state. At $U_{\text{eff}} = 2.75$ eV,
the magnetic moment of Co in the AFM3 state is about $2 \mu_B$, which is slightly higher than that of pure hcp Co, $1.715 \mu_B$ [51].

Fig. 9 shows the computed partial electronic density of states (DOS) of AFM3 \textit{Pnnm} \textit{Co}_2\textit{N} when $U_{\text{eff}} = 2.75$ eV. As expected, near the Fermi level, the Co $d$ orbitals mainly contribute to the DOS. A nonzero DOS is found at the Fermi level, indicating its metallic nature.

5. Conclusions

In this paper, we have carefully revisited the phase stability of \textit{Co}_2\textit{N} based on both experiments and first-principles calculations. PXRD measurements clearly confirm that the stable \textit{Co}_2\textit{N} crystal structure adopts the space group \textit{Pnnm} (isotype of \textit{h}-\textit{Fe}_2\textit{C} and \textit{Co}_2\textit{C}) and not \textit{Pbcn} (found for \textit{z}-\textit{Fe}_2\textit{N}). The refined structural parameters of \textit{Pnnm} \textit{Co}_2\textit{N} are $a = 4.6108(1) \text{Å}, b = 4.3498(1) \text{Å}, c = 2.85592(7) \text{Å}, x = 0.3242(1), y = 0.2643(1)$, with Co located at the 4\textit{g} site of $(x,y,0)$. Based on first-principles calculations, we have revealed that with pure DFT calculations a wrong crystal structure and a wrong magnetic state are obtained for \textit{Co}_2\textit{N} and that it is therefore essential to consider strong on-site electron correlation to correctly obtain the experimentally confirmed stable AFM \textit{Pnnm} \textit{Co}_2\textit{N} phase. In particular, an $U_{\text{eff}}$ value of around 2.75 eV provides the correct ground state and a formation energy consistent with experiments. It has also been found that the energetic stability is sensitive to the detailed magnetic ordering. Our considered AFM3 state (cf. Fig. 2) provides a reasonable description of the correct phase stability of \textit{Co}_2\textit{N} and thus can be used in future studies of cobalt nitrides and oxynitrides at modest computational costs.

CRediT authorship contribution statement

Yuji Ikeda: Investigation, Formal analysis, Writing - original draft, Visualization. Tanja S. Lehmann: Investigation, Formal analysis. Marc Widenmeyer: Investigation, Formal analysis, Data curation, Writing - original draft. Mauro Coduri: Resources, Writing - review & editing. Blazej Grabowski: Writing - review & editing, Supervision, Project administration. Rainer Niewa: Conceptualization, Writing - review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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