

Computational characterization of novel nanostructured materials: A case study of NiCl_2

Elizaveta B. Kalika,^{1,2} Alexey V. Verkhovtsev,³ Mikhail M. Maslov,^{4,2} Konstantin P. Katin,^{4,2} and Andrey V. Solov'yov³

¹*Moscow Institute of Physics and Technology, Institutskiy per. 9, Dolgoprudny, Moscow Region, 141700, Russia*

²*Research Institute for the Development of Scientific and Educational Potential of Youth, Aviatorov Str. 14/55, Moscow 119620, Russia*

³*MBN Research Center, Altenhöferallee 3, 60438 Frankfurt am Main, Germany*

⁴*National Research Nuclear University "MEPhI", Kashirskoe Shosse 31, Moscow, 115409, Russia*

A computational approach combining dispersion-corrected density functional theory (DFT) and classical molecular dynamics is employed to characterize the geometrical and thermo-mechanical properties of a recently proposed 2D transition metal dihalide NiCl_2 . The characterization is performed using a classical interatomic force field whose parameters are determined and verified through the comparison with the results of DFT calculations. The developed force field is used to study the mechanical response, thermal stability, and melting of a NiCl_2 monolayer on the atomistic level of detail. The 2D NiCl_2 sheet is found to be thermally stable at temperatures below its melting point of ~ 695 K. At higher temperatures, several subsequent structural transformations of NiCl_2 are observed, namely a transition into a porous 2D sheet and a 1D nanowire. The computational methodology presented through the case study of NiCl_2 can also be utilized to characterize other novel 2D materials, including recently synthesized NiO_2 , NiS_2 , and NiSe_2 .

I. INTRODUCTION

Nickel-based nanomaterials are considered promising for sensors, adsorbents, and catalysts. Recently synthesized Ni-based composites have proven their effectiveness as sensors for various organic and biological molecules [1–3]. Nickel nanoparticles possess catalytic activity for many reactions, including the synthesis of primary amines and hydrogen oxidation [4, 5]. Nickel-based two-dimensional (2D) materials can be used for the efficient generation of molecular oxygen [6, 7], electrocatalytic water splitting [8], and glucose oxidation [9]. In addition, recently synthesized pentagonal 2D sheets of nickel diazenide (NiN_2) have a tunable direct band gap and may serve as a precursor for pentagonal 2D materials [10].

Nickel-doped graphene materials are also widely used for many applications. In particular, they provide excellent sensing properties [11–13] and can effectively catalyze technologically important reactions, such as hydrogen production from water [14] and ethanol steam [15], oxygen reduction under alkaline conditions [16], and carbon monoxide reduction [17]. Another important application of Ni-doped graphene is hydrogen storage [18–20]. Due to 3d electrons and the spillover effect, nickel can hold hydrogen molecules. At the same time, graphene is not the only 2D material that can be doped with nickel. Other 2D materials, such as silicene, germanene and MoS_2 , have also been used as a substrate for nickel atoms and nanoparticles [21–23].

The aforementioned properties of Ni-doped 2D materials are based on a combination of the mechanical characteristics of a 2D sheet with the adsorption and catalytic properties of nickel. A further development of this idea is that nickel can be not only an alloying impurity but also the basis for a 2D material. Pure nickel does

not exist in the form of a 2D allotrope. However, an extensive computational search for layered crystals and related 2D materials [24] has recently predicted the existence of several 2D nickel-based materials of the composition NiX_2 ($X = \text{O}, \text{Cl}, \text{Br}, \text{I}, \text{S}, \text{and Se}$). Some of these materials have already been synthesized. Technologies developed for widespread 2D MoS_2 and MoSe_2 materials [25] and their analogs based on niobium [26], titanium [27] and tungsten [28] have been proven useful for synthesizing NiX_2 monolayers. Large-area NiO_2 monolayers separated by lanthanum atoms have been observed using scanning tunneling microscopy [29]. Recent experiments have proven the feasibility of chemical vapor deposition synthesis of nanometer-sized layers of NiCl_2 [30], NiS_2 [31], and NiSe_2 [32]. Moreover, NiCl_2 films up to four layers thick have been synthesized recently [30]. In all these materials, nickel atoms are organized in a regular 2D lattice so that the materials possess enhanced adsorption and catalytic properties.

Currently, there is limited experimental information on the properties of such 2D materials since only a few laboratories have synthesized them in limited quantities. Atomistic computer simulations can serve as a useful complementary approach to characterize the structure of such novel materials and explore their properties.

This paper presents the results of a computational characterization of a novel 2D material, NiCl_2 , using a multiscale modeling approach. NiCl_2 has been chosen as an illustrative and experimentally relevant representative of the Ni-based 2D materials family. A combination of quantum and classical approaches into a unified multiscale methodology permits a comprehensive investigation of the structure, mechanical properties, and thermal stability of NiCl_2 .

Density-functional theory (DFT) calculations provide reference data on the geometrical characteristics of the

2D NiCl_2 material. On this basis, a new classical interatomic potential is developed and benchmarked against the results of quantum-mechanical calculations. The validated potential is used for atomistic modeling of the mechanical and thermal stability of NiCl_2 using classical molecular dynamics (MD) employing the MBN Explorer [33] and MBN Studio [34] software packages.

Through an illustrative case study of NiCl_2 , we present a general methodology that can be utilized for the computational characterization of other novel materials, including the recently synthesized NiO_2 [29], NiS_2 [31], and NiSe_2 [32]. To the best of our knowledge, a 2D NiCl_2 has been studied computationally using DFT only in a few studies [35, 36], and there have been no MD-based studies of this material or other 2D nickel dihalides. The paper [35] studied the mechanical, electronic, and magnetic properties of monolayer and bilayer NiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) 2D structures. The recent study [36] investigated structural defects in NiCl_2 and similar materials and confirmed their stability in the environment using DFT calculations.

The paper is organized as follows. Section II describes the key aspects of theoretical methods utilized in DFT calculations and classical simulations. A particular focus is made on describing the procedure to determine the classical force field parameters for NiCl_2 . This follows with the discussion of the obtained results in Section III. The accuracy of the developed force field is evaluated in Section III A through the analysis of structural and energetic parameters of NiCl_2 . Section III B is devoted to the analysis of the mechanical properties of NiCl_2 by means of DFT and classical energy minimization calculations using the developed force field. In Section III C, the force field is utilized to study the thermal stability of NiCl_2 and evaluate its melting temperature using classical MD simulations. Finally, in Section IV, we draw a conclusion from this work and give an outlook for further developments in this research direction.

II. COMPUTATIONAL METHODOLOGY

A. DFT calculations

DFT calculations of the structural properties of a NiCl_2 sheet have been performed using the QUANTUM Espresso 6.5 software package [37, 38]. The plane-wave basis set for valence electron states, generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) functional form for the exchange-correlation energy [39], and projector-augmented-wave (PAW) pseudopotentials [40, 41] for core-electron interactions were used to perform the calculations. We have employed the kinetic energy cut-off for wave functions of 100 Ry (1360 eV) and kinetic energy cut-off for charge density and potential of 600 Ry (8160 eV) with checking the convergence of energy and charge to increase the simulation accuracy. In addition, the van der Waals interactions

have been considered through the D3 Grimme (DFT-D3) dispersion corrections [42]. The DFT-D3 approach possesses improved accuracy due to using environment-dependent dispersion coefficients and the inclusion of a three-body component to the dispersion correction energy term.

The distance between separate NiCl_2 sheets has been set equal to 30 Å, which provides sufficient space separation to avoid nonphysical interactions. Thus, optimization of the lattice parameter along the axis perpendicular to the NiCl_2 sheet plane was unnecessary. The atomic equilibrium positions have been obtained by the total energy minimization of the supercell using the calculated forces and stress on the atoms. The convergence criterion for self-consistent calculations for ionic relaxations was set to 10^{-10} eV between two consecutive steps. The geometry optimization of the NiCl_2 sheet was carried out without symmetry constraints until the Hellman-Feynman forces acting on the atoms became smaller than 10^{-4} hartree/bohr. Such criteria ensure that the absolute value of stress is less than 0.01 kbar. The parameters of the supercell have also been optimized. The first Brillouin zone integrations have been performed using the Monkhorst-Pack k -point sampling scheme [43] with the $6 \times 6 \times 1$ mesh grid and the Methfessel-Paxton smearing [44] with the smearing width of 0.02 Ry.

The NiCl_2 sheet is represented by a hexagonal $\text{Ni}_9\text{Cl}_{18}$ periodic cell containing 3×3 elementary NiCl_2 cells, see Fig. 1. The hexagonal symmetry corresponds to the results obtained earlier for this monolayer [24]. The lattice constant determined from the geometry optimization calculation is $a = 3a_0 = 10.328$ Å, where a_0 is the parameter of the NiCl_2 primitive unit cell. The equilibrium Ni-Cl bond length obtained from the DFT calculations is equal to 2.38 Å.

B. Classical MD simulations

Classical geometry optimization calculations and MD simulations have been performed by means of MBN Explorer [33] – a software package for multiscale modeling of complex molecular structures and dynamics. MBN Explorer permits the simulation of a wide range of Meso-Bio-Nano (MBN) systems [45, 46], including nanosystems, nanostructured materials, as well as composite and hybrid materials with sizes ranging from atomic to mesoscopic [47–52]. The dedicated MBN Studio toolkit [34] has been utilized to create the systems, prepare all necessary input files, and analyze and visualize simulation outputs.

C. Determination of the classical force field for NiCl_2

The first part of this study has been devoted to determining the parameters of a classical force field for NiCl_2 .

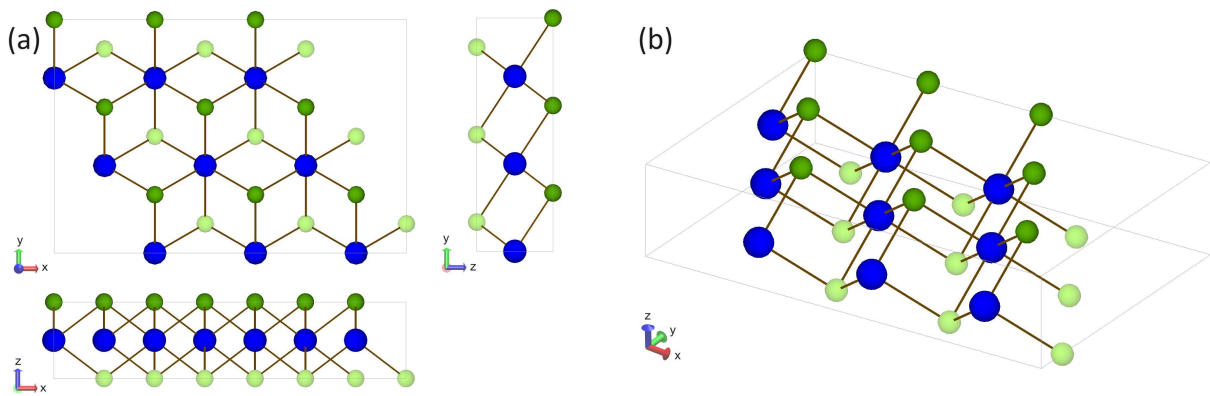


FIG. 1. Structure of a NiCl_2 supercell used in the DFT calculations. The supercell contains 9 nickel and 18 chlorine atoms, shown in blue and green (dark and light) colors, respectively. Chlorine atoms in the top and bottom atomic layers are shown by dark-green and light-green colors, respectively. Panel (a) shows three orthographic projections of the considered supercell – top and side views (top row) and a front view (bottom row). Panel (b) shows a 3-dimensional projection of the supercell.

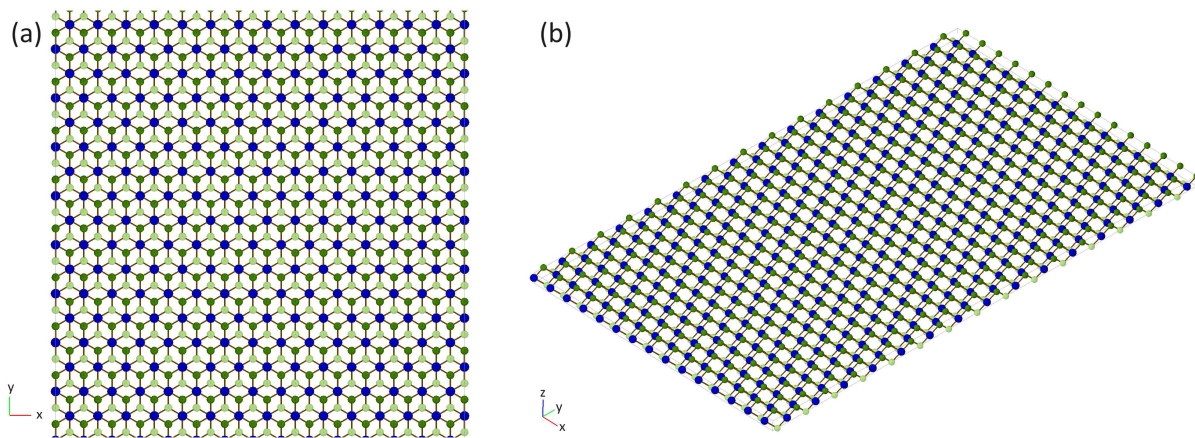


FIG. 2. Structure of a NiCl_2 sheet used in classical MD simulations. Panel (a) shows the top view of a fragment of a NiCl_2 sheet, while panel (b) shows a 3-dimensional projection of the entire system containing 1350 atoms. Ni and Cl atoms are shown in blue and green colors, respectively. Cl atoms in the top and bottom atomic layers are shown by dark-green and light-green colors, respectively.

The geometry of the NiCl_2 supercell obtained after DFT-based optimization (see Fig. 1) was taken as an initial geometry for the calculations using the classical force field. The NiCl_2 supercell was translated in space along the translation vectors, and the generated crystal was cut to fill in a rectangular simulation box, which was replicated in space using periodic boundary conditions. The resulting structure of a 2D NiCl_2 system is shown in Fig. 2. The simulation box used for the classical simulations has the size of $52.08 \text{ \AA} \times 90.30 \text{ \AA} \times 100.00 \text{ \AA}$ and contains 1350 atoms.

1. Determination of parameters through classical MD simulations

As a first educated guess, several MD simulations have been carried out with trial force field parameters fitted

for other transitional metal halides NiF_2 [53], ZnCl_2 [54], and FeCl_3 [55]. The force field employed in these simulations has been constructed as a sum of the short-term exponential, long-term r^{-6} power, and the Coulomb potentials. Such force fields have been commonly utilized in MD simulations of metal halides and oxides, as well as various ionic crystals and other ionocovalent systems (e.g. glasses) [56–59]. The NiCl_2 system was unstable with any considered trial parameters; the sheet lost its planarity and became strongly bent using the considered force field potentials.

Therefore, a new set of classical force field parameters for the 2D NiCl_2 system has been determined in this study as follows. The Nelder-Mead algorithm [60] has been utilized to optimize the force field parameters. The algorithm is simplex-based, meaning that in a n -dimensional space, it maintains a set of $n + 1$ points called simplex. After calculating the value of the function

at each point of the simplex, the algorithm extrapolates the function's behavior to find a new test point and replaces the test points with the worst result with a new one. This process continues until the result converges to the pre-defined tolerance value or reaches the maximum number of iterations. The Nelder-Mead algorithm was implemented in Python via `scipy.optimize.minimize` library [61]. This algorithm was used to fit the geometrical parameters of NiCl_2 calculated using MBN Explorer [33] to the corresponding parameters obtained through the DFT-based structure optimization; results of this analysis are presented below in Sect. III A.

NiCl_2 is an ionic crystal where polarization effects due to the ions of opposite charges may play a significant role. Several computational approaches for describing the ion-induced polarization interaction in various molecular systems within the classical MD framework have been discussed in the literature, including the addition of a r^{-4} term to a r^{-6} long-range potential [62–64] or considering a r^{-4} term as the only contribution to the long-range interaction [65, 66]. In this study, we have used the latter approach for the sake of minimizing the number of force field parameters to be determined. The resulting total interaction potential between atoms i and j of the system is given by the following expression:

$$U(r_{ij}) = A_{ij} e^{-\alpha_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^4} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

As shown below in Sections III A and III B, the force field given by Eq. (1) provides a good overall agreement with the results of DFT calculations regarding the structural and mechanical properties of a 2D NiCl_2 material.

Six parameters of the force field, Eq. (1), have been optimized using the Nelder-Mead algorithm: $A_{\text{Ni-Cl}}$, $\alpha_{\text{Ni-Cl}}$, $A_{\text{Cl-Cl}}$, $\alpha_{\text{Cl-Cl}}$, $C_{\text{Cl-Cl}}$ and q_{Cl} . Partial charges on Ni and Cl atoms have been set to ensure the system is electrically neutral, so that $|q_{\text{Ni}}| = 2|q_{\text{Cl}}|$. Following the approach adopted in several earlier studies [53, 67–70] for a number of ionic crystals and ionocovalent systems, we have not considered the non-Coulombic contributions between the positively charged (in our case, nickel) ions, i.e. $A_{\text{Ni-Ni}} = 0$ and $C_{\text{Ni-Ni}} = 0$. Following the considerations made in Ref. [68], the large partial atomic charge on the cations ensures that they are always well separated from each other, and their repulsive and van der Waals interactions can be neglected. The parameter $C_{\text{Ni-Cl}}$ for the long-range interaction between the ions of different signs was also set equal to zero (see e.g. Refs. [53–55]) on the grounds that unlike (i.e. Ni and Cl) nearest neighbours are close enough for the van der Waals interaction to be quenched [67, 68]. A 7 Å cutoff was applied for the exponential and power terms of the potential. The Coulomb potential was calculated using the Ewald summation method [71, 72] with the cutoff of 12 Å. MD simulations with a simulation time of 30 ps and a time step of 1 fs, Langevin thermostat temperature of 300 K, and damping time of 0.1 ps were performed for each generated set of parameters.

TABLE I. Parameters of the force field, Eq. (1), derived in this study for the description of a 2D NiCl_2 material (see the main text for details).

	A_{ij} (eV)	α_{ij} ($\text{\AA}^{-1}$)	C (eV $\text{\AA}^4$)		$q, e $
Ni-Cl	10715.83	5.034	–	Ni	1.34
Cl-Cl	1439.08	3.494	0.779	Cl	–0.67

The following geometrical parameters of NiCl_2 have been compared to the results of DFT calculations: (i) Ni-Cl bond length ($d_{\text{Ni-Cl}}$); (ii) Ni-Ni bond length ($d_{\text{Ni-Ni}}$); (iii) in-plane Cl-Cl bond length ($d_{\text{Cl-Cl}}$); and (iv) the interplanar Cl-Ni-Cl angle ($\varphi_{\text{Cl-Ni-Cl}}$), denoted hereafter as φ for brevity. In addition, the system's energy as a function of the Ni-Cl interplanar distance l has also been analyzed. The distance between the Ni and Cl atomic planes was gradually varied, and single-point energy calculations were carried out using MBN Explorer for different values of l . The resulting dependence of the system's energy on the Ni-Cl interplanar distance was fitted by a quadratic function. The value of l corresponding to the minimum system's energy was determined from classical force field calculations and compared to the results of DFT calculations. Then, the standard deviation

$$\sigma = \sqrt{\sum_i \left(\frac{d_i - d_i^{\text{DFT}}}{d_i^{\text{DFT}}} \right)^2 + \left(\frac{\varphi - \varphi^{\text{DFT}}}{\varphi^{\text{DFT}}} \right)^2 + \left(\frac{l - l^{\text{DFT}}}{l^{\text{DFT}}} \right)^2} \quad (2)$$

was calculated and minimized using the Nelder-Mead algorithm [60]. Here, the summation has been carried out over all Ni-Ni, Ni-Cl and Cl-Cl covalent bonds of the system. Each round of force field parameter optimization consisted of 30 iterations, and the parameters resulting from each optimization round were used as the starting parameters for the following one. 400 subsequent optimization rounds have been performed to determine the parameters of the force field. The force field parameters obtained via classical MD simulations performed at 300 K are listed in Table III in Appendix.

2. Determination of parameters through structure optimization calculations

Due to relatively long simulation times, the MD-based procedure described in the previous section is inefficient for scanning a multidimensional parameter surface over a broad range of parameters. Therefore, the second round of force field parameter optimization was performed through a series of classical structure optimization calculations. The parameters generated at the previous step (see Sect. II C 1 and Table III in Appendix) were used as a starting point. Similarly to the previous step, the force field optimization procedure was performed using the Nelder-Mead algorithm [60]. Classical structure

optimization calculations were performed using the velocity quenching algorithm for 5000 optimization steps with a time step of 0.1 fs.

A much shorter computational time of a structure optimization calculation than an MD simulation has allowed us to explore a broader range of force field parameter values. However, it was observed that the optimization of all force field parameters, including partial charges, produces unrealistic non-physical values of partial charges (much larger than the formal charges of +2 and -1 on Ni and Cl atoms, respectively) due to lowering the total potential energy of the system with an increase of attractive electrostatic interaction between positively charged Ni atoms and negatively charged Cl atoms. In order to avoid this non-physical behavior, partial charges on Ni and Cl have been considered as fixed parameters (ensuring the total charge of the whole system is zero), and ten independent rounds of force field parameter optimization have been performed with constant values of atomic partial charges q_{Cl} in the range from $-0.859|e|$ to $-0.5|e|$. The force field parameters obtained after each round of structure optimization calculations were tested by analyzing the stability and planarity of the NiCl_2 system over a one-nanosecond-long MD simulation at 300 K. The final choice of the atomic partial charges was made to get the closest correspondence to the DFT-based results on the geometrical and mechanical properties of the 2D NiCl_2 system, as described below in Sections III A and III B.

It should be noted that the question of choosing atomic partial charges for the description of ionic crystals and other ionocovalent systems (such as silicate glasses) has been discussed in the literature, see e.g. Ref. [73] and references therein. MD simulations of SiO_2 systems showed that using formal charges (i.e., +4 for Si and -2 for O atoms) requires the use of additional angular 3-body energy terms to properly describe the system's geometry [74]. Therefore, a commonly adopted approach for simulating ionocovalent systems is to use partial (rather than formal) atomic charges that are treated as an additional fitting parameter [69, 70, 75] in order to reproduce the correct system's geometry without introducing additional energy terms to the empirical force field. This approach has been adopted in the present study to determine the partial charges on nickel and chlorine atoms.

The final values of the force field parameters and atomic partial charges for NiCl_2 , derived from the comparison of NiCl_2 geometrical parameters to the DFT results, are listed in Table I. These values have been employed in all the simulations described below in Section III.

III. RESULTS AND DISCUSSION

A. Evaluation of the accuracy of the constructed force field

NiCl_2 is a novel 2D material for which little information has been obtained experimentally and computationally. Hence, it is important to evaluate the accuracy of the developed classical force field in order to make computational predictions of the structural and thermo-mechanical properties of NiCl_2 .

Table II lists the values of Ni-Cl, Ni-Ni and Cl-Cl bond lengths ($d_{\text{Ni-Cl}}$, $d_{\text{Ni-Ni}}$ and $d_{\text{Cl-Cl}}$) as well as the Cl-Cl interplanar distance ($l_{\text{Cl-Cl}}$) and the Cl-Ni-Cl angle ($\varphi_{\text{Cl-Ni-Cl}}$) obtained in this study by means of classical force field optimization (column labeled 'FF') and DFT optimization calculations using the PBE exchange-correlation functional. The present results are compared with several recent DFT calculations of a free 2D NiCl_2 monolayer [35, 36] and that encapsulated inside a metal-organic framework [76].

TABLE II. Comparison of geometrical parameters of a NiCl_2 2D sheet after geometry optimization using the classical force field, Eq. (1) (column labeled 'FF'), and DFT using the PBE exchange-correlation functional. The results obtained in this study are also compared with the results of recent DFT calculations [35, 36, 76].

Optimization method	FF	DFT			
		this work	Ref. [36]	Ref. [35]	Ref. [76]
$d_{\text{Ni-Cl}}$, Å	2.24	2.38	2.38	2.42	2.42
$d_{\text{Ni-Ni}}$, Å	3.57	3.44			3.56
$d_{\text{Cl-Cl}}$ (in-plane), Å	3.47	3.44			
$l_{\text{Cl-Cl}}$ (interplanar), Å	2.68	3.28		2.65	
$\varphi_{\text{Cl-Ni-Cl}}$, deg	73.5	87.2			

The results listed in Table II indicate a good overall agreement (with the relative discrepancy of $\sim 5\%$) between the outcomes of classical structure optimization calculations and the DFT calculations performed in this study and reported in the literature [35, 36, 76]. The interlayer vertical distance between two chlorine planes, $l_{\text{Cl-Cl}}$, obtained from the classical calculations is about 20% shorter than the values obtained by DFT, while being in good agreement with the results of the recent DFT-based study [35]. A smaller Cl-Cl interplanar distance results in smaller values of the angles $\varphi_{\text{Cl-Ni-Cl}}$ compared to the outcomes of DFT calculations.

Overall, the classical force field, Eq. (1), with the parameters listed in Table I describes with reasonable accuracy the geometrical parameters of a 2D NiCl_2 sheet. The range of discrepancies between the results of classical force field-based and DFT-based geometry optimization calculations is similar to that obtained in earlier studies of transition-metal clusters and bulk materials [48, 77].

B. Mechanical properties of NiCl₂

In this study, the mechanical properties of a NiCl₂ sheet have been analyzed by both DFT and classical force field calculations. DFT-based calculations have used, as an input, the optimized NiCl₂ supercell described above in Section II A.

The uniform stretching of the NiCl₂ sheet has been simulated by simultaneously increasing the lattice parameters of the supercell along the x - and y -directions (parallel to the NiCl₂ plane) and further optimizing atomic positions in the supercell. Classical geometry optimization calculations were performed by means of MBN Explorer [33] using the velocity quenching algorithm for 20,000 optimization steps with a time step of 1 fs.

During the biaxial stretching, the lattice constant a increases as

$$a = a_0(1 + \varepsilon) , \quad (3)$$

where a_0 is the equilibrium lattice constant and ε is the relative deformation (strain). The deformation energy ΔE has been calculated as follows:

$$\Delta E = E - E_0 , \quad (4)$$

where E is the total potential energy of the deformed system and E_0 is the potential energy of the unperturbed system. As the simulation boxes considered in the DFT-based and classical force field optimization calculations contain different numbers of atoms, the calculated deformation energy was divided by the number of NiCl₂ units in the respective simulation box.

Figure 3(a) shows the dependence of the NiCl₂ sheet deformation energy on strain ε . In the region of small deformations (for strain values $\varepsilon \lesssim 0.05$), the dependence of deformation energy on ε follows a quadratic dependence, indicative of the elastic deformation. At larger deformations, the calculated dependence starts to deviate from the quadratic dependence. The calculations employing the classical force field, Eq. (1), predict the deformation threshold at $\varepsilon \sim 0.11$, when the 2D sheet breaks into smaller “islands” (see Fig. 3(b)), which causes a sharp drop in the potential energy of the system and, hence, in its deformation energy.

The mechanical properties of 2D materials are commonly characterized via the 2D Young’s modulus E_{2D} , which does not depend on the sheet thickness in contrast to the “conventional” 3D Young’s modulus [78–80]. The 2D Young’s modulus is calculated as

$$E_{2D} = \frac{1}{2S_0} (\Delta E)'' , \quad (5)$$

where S_0 is the surface area of the relaxed 2D system and $(\Delta E)''$ is the second derivative of the deformation energy with respect to biaxial deformation ε . A quadratic fit to the dependence of system’s total deformation energy on ε , calculated by means of DFT, yields the value $E_{2D} =$

50.1 N/m. The classical force field, Eq. (1), predicts a close value of 51.8 N/m. These values are in agreement with the value $E_{2D} = 54$ N/m, obtained for NiCl₂ using DFT calculations in Ref. [35]. Similar values of the 2D Young’s modulus were reported in the cited study [35] for related Ni-based 2D materials, NiBr₂ (50 N/m) and NiI₂ (45 N/m). These results indicate that 2D NiCl₂ and other nickel dihalides are less rigid materials compared to other well-studied 2D sheets like graphene or MoS₂, which have the 2D Young’s modulus of ~ 340 N/m and 170 N/m, respectively [81, 82].

To estimate the “conventional” 3D Young’s modulus, the obtained value E_{2D} should be divided by the effective sheet thickness h . According to the results obtained using the classical force field, Eq. (1), the NiCl₂ sheet thickness (that is, the distance l_{Cl-Cl} between the chlorine planes) is equal to 2.68 Å. The interlayer distance between the adjacent layers of NiCl₂ equals 3.08 Å [35] so that the effective sheet thickness can be estimated as $h = 5.76$ Å. Using this value, one obtains the 3D Young’s modulus $E_{3D} = E_{2D}/h \approx 90$ GPa.

C. Melting temperature and thermal stability of NiCl₂

The interatomic force field described in Sect. II C has been utilized to study the thermal properties of a 2D NiCl₂ sheet and evaluate its melting temperature. This has been done by conducting a series of constant temperature MD simulations as follows. The optimized structure of NiCl₂ was heated gradually by 50 degrees (in the temperature range from 0 to 650 K) or by 100 degrees (in the range from 800 to 3200 K) over 200 ps and then equilibrated over 1 ns at each temperature. In order to avoid any artifacts related to the incomplete thermalization of the system, the first 400 ps of each trajectory simulated at a given temperature were excluded from the analysis. The average value of system’s total energy at a given temperature was determined over the last 600-ps part of each trajectory. A smaller temperature increment of 10 K has been considered in the temperature range from 650 to 800 K where the melting phase transition occurs (see below). In this case, 10 ns-long simulations were performed at each temperature, and the system’s total energy was analyzed over the last 6 ns of the simulated trajectories. The resulting caloric curve, that is the dependence of the time-averaged total energy of the system on temperature, $\langle E_{tot} \rangle(T)$, is shown in Fig. 4(a) by symbols. Figure 4(b) shows the temperature dependence of heat capacity at constant volume C_v , defined as a derivative of the internal energy of the system over temperature:

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v . \quad (6)$$

The melting process in a macroscopic system occurs at a specific temperature and reveals itself as a first-order

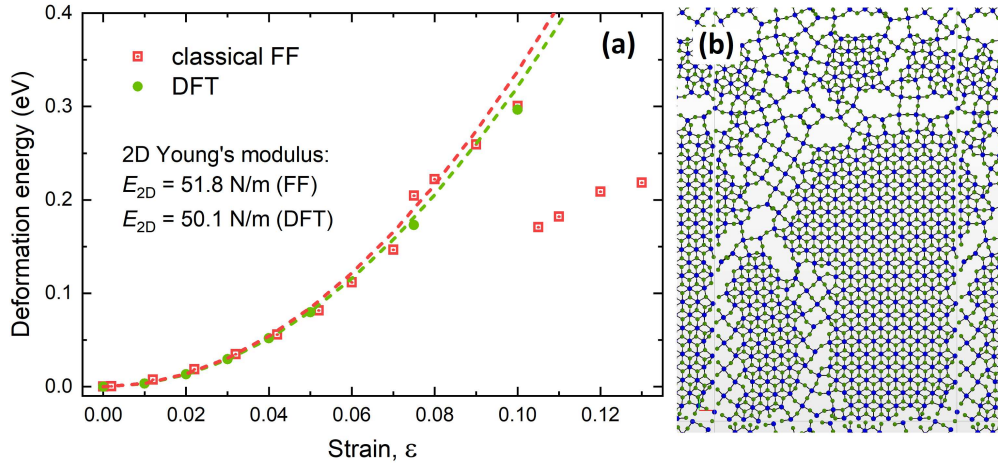


FIG. 3. Panel (a): Deformation energy ΔE of a biaxially stretched NiCl_2 sheet as a function of relative deformation ϵ . Classical geometry optimization calculations (red symbols) have been performed using the force field, Eq. (1), and the parameters listed in Table I. Panel (b): Structure of NiCl_2 at strain $\epsilon = 0.11$, which corresponds to the mechanical stability threshold for this material as predicted by the classical force field calculations. Ni and Cl atoms are shown in blue and green colors, respectively.

phase transition via a spike in the heat capacity of the system at the transition temperature.

At the initial phase of NiCl_2 heating, the system's total energy grows linearly with temperature; see the inset in Fig. 4(a). At temperatures above ~ 600 K the crystalline structure of the NiCl_2 sheet is strongly deformed, but the system maintains its integrity. A jump in the system's total energy has been observed at temperatures between 680 and 700 K. The calculated heat capacity curve has a sharp maximum at $T \approx 695$ K, indicating the melting temperature of NiCl_2 . This value is lower than the melting temperature for bulk nickel, $T_m(\text{Ni}) = 1728$ K, and of bulk NiCl_2 , $T_m(\text{NiCl}_2^{\text{bulk}}) = 1274$ K [83]. At the same time, the evaluated melting temperature of 2D NiCl_2 is within the temperature range ($T \sim 500 - 1000$ K) where other 2D metal halides, such as NaCl , become thermally unstable and lose their structural integrity, as determined computationally from *ab initio* MD simulations [84].

At temperatures above the melting point, the system's total energy $\langle E_{\text{tot}} \rangle$ continues to grow linearly with T (see the inset in Fig. 4(a)) until the onset of another structural transformation emerges at $T \sim 1500$ K. In contrast to the melting phase transition at $T_m \approx 695$ K, this high-temperature transformation takes place over a broad temperature range from approximately 1500 to 2700 K, as indicated by the deviation of the $\langle E_{\text{tot}} \rangle(T)$ dependence from a linear function and a peak in the $C_v(T)$ dependence in the temperature range $\sim 2400 - 2700$ K. This transition corresponds to the evaporation of NiCl_2 fragments from a 1D NiCl_2 nanowire (see the discussion below).

The structural transformations corresponding to the peaks in the heat capacity curve can be visualized by analyzing the radial distribution function (RDF) of atoms in the system. The RDF characterizes the number of atoms located at a certain radial distance r from a refer-

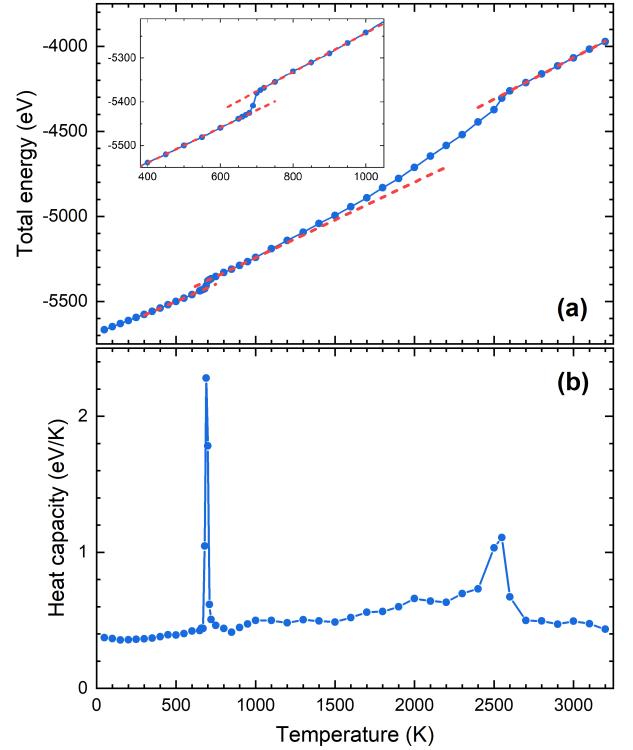


FIG. 4. Caloric curve for a 2D NiCl_2 material (panel (a)) and the corresponding heat capacity C_v as a function of temperature (panel (b)) obtained using classical MD simulations. The peak in the $C_v(T)$ dependence at $T \approx 695$ K indicates the melting temperature of NiCl_2 . A broader peak centered at $T \sim 2500$ K indicates a sublimation into the gas of NiCl_2 molecules and small atomic and molecular fragments (see the main text for details).

ence atom. The RDF for Ni-Ni and Cl-Cl atomic pairs,

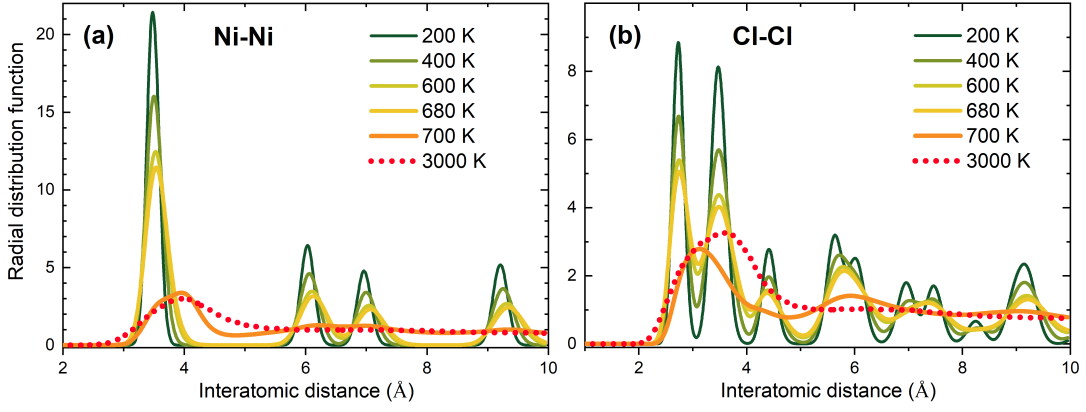


FIG. 5. Radial distribution function for (a) nickel and (b) chlorine atoms of NiCl_2 at different temperatures of the system. A rapid change of the RDFs between 680 and 700 K indicates the melting phase transition.

evaluated at different temperatures of the system, are plotted in Figures 5(a) and 5(b), respectively. A rapid change of the RDFs between 680 and 700 K indicates the melting phase transition.

It is of particular interest to explore in more detail the phase transition from the crystalline NiCl_2 to its molten state. Figure 6 shows the variation of the system's total energy, E_{tot} , as a function of simulation time t ; the first 8 ns of the simulations (out of 10 ns) are shown for better clarity. Colored curves show the $E_{\text{tot}}(t)$ dependencies for three different temperatures, namely $T = 670$ K (below the phase transition temperature), $T = 700$ K (in the phase transition region), and $T = 780$ K (above the phase transition temperature).

At $T = 670$ K (black curve in Fig. 6), the total energy of NiCl_2 fluctuates around the average value of about -5430 eV, which indicates that the system is thermally stable at this temperature over the considered simulation time. At $T = 700$ K (red curve in Fig. 6), the system's energy stays nearly constant within the first ~ 0.7 ns of the simulated trajectory, followed by a rapid rise of $E_{\text{tot}}(t)$ within the next ~ 0.4 ns. This jump in the total energy is attributed to the formation of defects (holes) in the NiCl_2 sheet, as shown in Fig. 7(c). After that, the system's total energy decreases as the system relaxes into a porous 2D structure, see Fig. 7(d,e). The structure shown in Fig. 7(e) is metastable and evolves into a different 2D structure, where denser regions are connected by thin NiCl_2 links, see Fig. 7(f). It should be noted that the results presented in Figures 6 and 7 have been obtained for the NiCl_2 sheet of a particular size, containing 1350 atoms. A detailed analysis of the system's size on its thermal properties and the observed structural transformations is an interesting topic which, however, goes beyond the scope of the present study.

The structure shown in Fig. 7(f) is stable at $T = 700$ K over a 10 ns-long simulation. However, the “dissolution” of the thin NiCl_2 links seen in Fig. 7(f) might take place on a longer time scale, leading to the formation of a 1D structure. Analyzing the dynamics of the NiCl_2 system

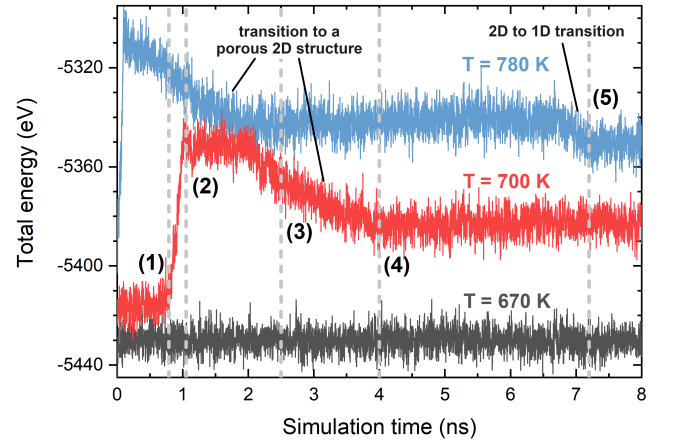


FIG. 6. Variation of the system's total energy, E_{tot} , as a function of simulation time t . Colored curves show the $E_{\text{tot}}(t)$ dependencies for different temperatures, namely $T = 670$ K (below the phase transition temperature), $T = 700$ K (in the phase transition region), and $T = 780$ K (above the phase transition temperature). Labels (1) to (4) correspond to different time instants (dashed lines) for the curve at $T = 700$ K, while label (5) indicates the time instant for the curve at $T = 780$ K. These instants (1)–(5) correspond to the system's snapshots shown in panels (c)–(g) of Fig. 7.

at higher temperatures enables to observe a 2D-to-1D structural transformation within the considered simulation times. Indeed, at $T = 780$ K, the NiCl_2 system transforms into a 1D nanowire (see Fig. 7(g)), which is thermally stable at temperatures below ~ 1500 K within the considered simulation times. This transformation is characterized by a decrease of the system's total energy, see the blue curve in Fig. 6.

At temperatures of ~ 1500 K, NiCl_2 monomers begin to evaporate from the NiCl_2 nanowire (see Fig. 8(a)), which causes a deviation from the linear dependence in the caloric curve shown in Fig. 4(a). As the temperature increases, more NiCl_2 units detach from the nanowire,

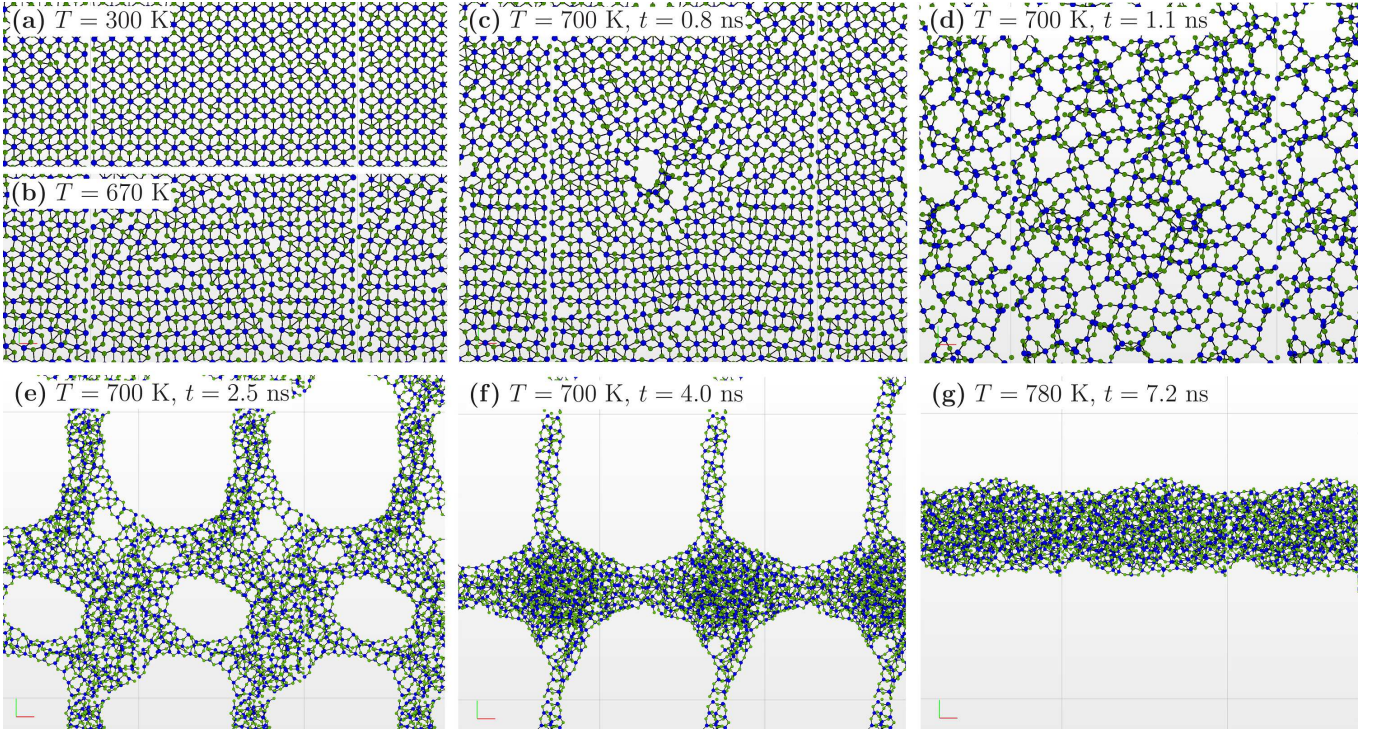


FIG. 7. Snapshots of the NiCl_2 system at different temperatures T as indicated. Nickel and chlorine atoms are shown in blue and green colors, respectively. Panels (c) to (g) illustrate the system's structure at different time instants corresponding to labels (1)–(5) in Fig. 6.

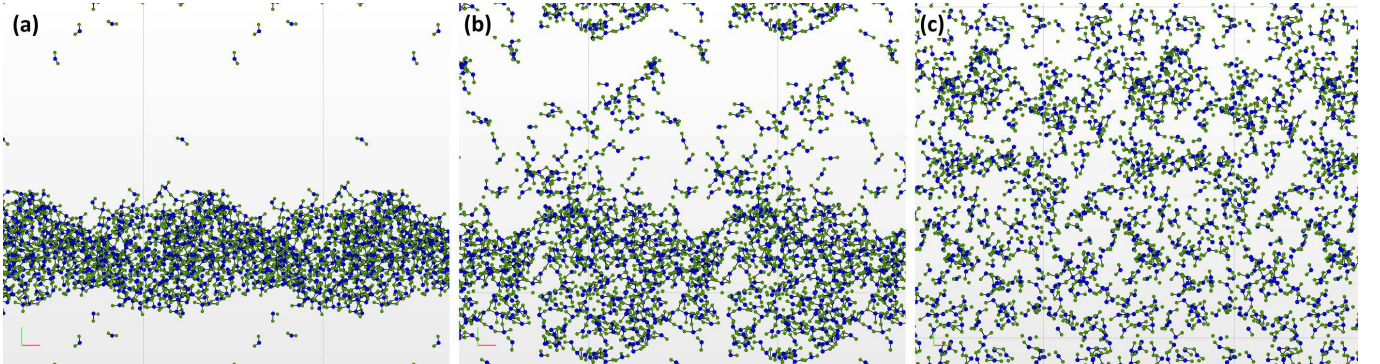


FIG. 8. Snapshots of the NiCl_2 system at temperatures $T = 1800$ K (a), 2400 K (b) and 3000 K (c) at the end of 1-nanosecond-long simulations. As the temperature increases, more NiCl_2 units are evaporated from the 1D NiCl_2 nanowire [see Fig. 7(g)], leading to its sublimation into a gas of NiCl_2 molecules and smaller fragments such as NiCl and isolated Ni and Cl atoms at $T \sim 2550$ K. Nickel and chlorine atoms are shown in blue and green colors, respectively.

resulting in the sublimation of the nanowire into a gas of NiCl_2 molecules and smaller fragments such as NiCl dimers and isolated Ni and Cl atoms, see Fig. 8(b,c). This phenomenon is characterized by the change of the $\langle E_{\text{tot}} \rangle(T)$ slope shown in Fig. 4(a) and a peak in the heat capacity curve centered at $T \approx 2550$ K.

IV. CONCLUSIONS

Two-dimensional (2D) materials possess unique technologically-relevant properties, which are often quite different from the properties of the corresponding bulk counterparts. Monolayers of layered crystals are particularly interesting because they can be synthesized with a well-known ‘top-down’ approach. Extensive experimental characterization of such materials is expensive and time-consuming, while computational modeling may provide valuable support for experimental research.

This study has reported results of a computer simulation of the recently proposed novel 2D material NiCl_2 by means of DFT calculations and classical MD simulations. In order to characterize the geometrical and thermo-mechanical properties of the 2D NiCl_2 system, a classical interatomic force field was developed and verified through the comparison with the results of DFT calculations.

The combination of a DFT approach and a classical approach based on an interatomic force field provides insight into the structural and thermo-mechanical properties of the 2D NiCl_2 material. It has been found that the NiCl_2 sheet is mechanically stable upon biaxial stretching at the relative deformation up to 11%. 2D Young's modulus for NiCl_2 obtained by DFT calculations and calculations employing the classical force field is ~ 50 N/m, in agreement with the results of recent DFT calculations [35]. The Young's modulus for a 2D NiCl_2 system is about 5 – 10 times lower than Young's modulus of other commonly studied 2D materials such as graphene, MoS_2 and WS_2 . The performed MD simulations indicate that the NiCl_2 sheet is thermally stable up to the melting point temperature of ~ 695 K. At temperatures above the melting point, structural degradation of NiCl_2 has been observed, which involves several subsequent structural transformations into a porous 2D sheet, a 1D nanowire, and a sublimation into a gas of NiCl_2 monomers and one- and two-atom fragments.

The classical force field developed in this study for simulating the 2D NiCl_2 material describes reasonably accurately the geometrical parameters of NiCl_2 , determined on the basis of DFT calculations. The force field parameters for NiCl_2 presented in this study might be useful for studying other characteristics of this material, such as

thermal conductivity, elastic constants, or phonon dispersion curves. Finally, the methodology presented through an illustrative case study of NiCl_2 can also be utilized for the computational characterization of other novel 2D materials, including recently synthesized NiO_2 , NiS_2 and NiSe_2 materials.

APPENDIX

Table III lists trial parameters of the force field for a 2D NiCl_2 material, Eq. (1), derived in this study through a series of constant-temperature MD simulations (see Sect. II C 1 for details).

TABLE III. Trial parameters of the force field for a 2D NiCl_2 material, Eq. (1), derived in this study through a series of constant-temperature MD simulations.

	A_{ij} (eV)	α_{ij} ($\text{\AA}^{-1}$)	C (eV $\text{\AA}^4$)		$q, e $
Ni-Cl	10804.52	4.73	—	Ni	1.718
Cl-Cl	1465.99	3.55	0.805	Cl	-0.859

ACKNOWLEDGEMENTS

The authors acknowledge the support of this work by the Deutsche Forschungsgemeinschaft (DFG), project no. 452691275. The possibility of performing computer simulations at the Goethe-HLR cluster of the Frankfurt Center for Scientific Computing (CSC) is also gratefully acknowledged.

-
- [1] P. Deng, X. Nie, Y. Wu, Y. Tian, J. Li, and Q. He, *Microchem. J.* **160**, 105744 (2021).
 - [2] H. Karimi-Maleh, K. Cellat, K. Arkan, A. Savk, F. Karimi, and F. Şen, *Mater. Chem. Phys.* **250**, 123042 (2020).
 - [3] R. Ahmad, T. Bedük, S. M. Majhi, and K. N. Salama, *Sens. Actuators B Chem.* **286**, 139 (2019).
 - [4] R. Jagadeesh, K. Murugesan, and M. Beller, *Angew. Chem. Int. Ed.* **58**, 5064 (2019).
 - [5] A. G. Oshchepkov, A. Bonnefont, S. N. Pronkin, O. V. Cherstiouk, C. Ulhaq-Bouillet, V. Papaefthimiou, V. N. Parmon, and E. R. Savinova, *J. Power Sources* **402**, 447 (2018).
 - [6] C. Luan, G. Liu, Y. Liu, L. Yu, Y. Wang, Y. Xiao, H. Qiao, X. Dai, and X. Zhang, *ACS Nano* **12**, 3875 (2018).
 - [7] Y. Wang, Y. Zhou, M. Han, Y. Xi, H. You, H. Xianfeng, Z. Li, J. Zhou, D. Song, D. Wang, and F. Gao, *Small* **15**, 1805435 (2019).
 - [8] Q. Liang, L. Zhong, C. Du, Y. Luo, J. Zhao, Y. Zheng, J. Xu, J. Ma, C. Liu, S. Li, and Q. Yan, *ACS Nano* **13**, 7975 (2019).
 - [9] Y. Shu, B. Li, J. Chen, Q. Xu, H. Pang, and X. Hu, *ACS Appl. Mater. Interfaces* **10**, 2360 (2018).
 - [10] M. Bykov, E. Bykova, A. V. Ponomareva, F. Tasnádi, S. Chariton, V. B. Prakapenka, K. Glazyrin, J. S. Smith, M. F. Mahmood, I. A. Abrikosov, and A. F. Goncharov, *ACS Nano* **15**, 13539 (2021).
 - [11] D.-T. Phan and G.-S. Chung, *Int. J. Hydrogen Energy* **39**, 20294 (2014).
 - [12] Z. Ren, H. Mao, H. Luo, and Y. Liu, *Carbon* **149**, 609 (2019).
 - [13] G. Deokar, J. Casanova-Cháfer, N. S. Rajput, C. Aubry, E. Llobet, M. Jouiad, and P. M. Costa, *Sens. Actuators B Chem.* **305**, 127458 (2020).
 - [14] W. Zhang, Y. Li, and S. Peng, *J. Mater. Chem. A* **5**, 13072 (2017).
 - [15] D. Chen, W. Wang, and C. Liu, *Int. J. Hydrogen Energy* **44**, 6560 (2019).
 - [16] R. J. Toh, H. L. Poh, Z. Sofer, and M. Pumera, *Chem. Asian J.* **8**, 1295 (2013).
 - [17] X.-Y. Xu, J. Li, H. Xu, X. Xu, and C. Zhao, *New J. Chem.* **40**, 9361 (2016).

- [18] C. Zhou, J. A. Szpunar, and X. Cui, *ACS Appl. Mater. Interfaces* **8**, 15232 (2016).
- [19] D. Zhou, K. Cui, Z. Zhou, C. Liu, W. Zhao, P. Li, and X. Qu, *Int. J. Hydrogen Energy* **46**, 34369 (2021).
- [20] L. R. Safina, K. A. Krylova, R. T. Murzaev, J. A. Bainova, and R. R. Mulyukov, *Materials* **14**, 2098 (2021).
- [21] A. Manjanath, V. Kumar, and A. K. Singh, *Phys. Chem. Chem. Phys.* **16**, 1667 (2014).
- [22] S. Li, J.-C. Ren, Z. Ao, and W. Liu, *Chem. Phys. Lett.* **706**, 202 (2018).
- [23] Y. Li, X. Zhang, D. Chen, S. Xiao, and J. Tang, *Appl. Surf. Sci.* **443**, 274 (2018).
- [24] N. Mounet, M. Gibertini, P. Schwaller, D. Campi, A. Merkys, A. Marrazzo, T. Sohier, I. E. Castelli, A. Cepellotti, G. Pizzi, and N. Marzari, *Nature Nanotechnol.* **13**, 246 (2018).
- [25] K. M. McCreary, A. T. Hanbicki, J. T. Robinson, E. Cobas, J. C. Culbertson, A. L. Friedman, G. G. Jernigan, and B. T. Jonker, *Adv. Funct. Mater.* **24**, 6449 (2014).
- [26] H. Wang, X. Huang, J. Lin, J. Cui, Y. Chen, C. Zhu, F. Liu, Q. Zeng, J. Zhou, P. Yu, X. Wang, H. He, S. H. Tsang, W. Gao, K. Suenaga, F. Ma, C. Yang, L. Lu, T. Yu, E. H. T. Teo, G. Liu, and Z. Liu, *Nature Commun.* **8**, 394 (2017).
- [27] P. C. Sherrell, K. Sharda, C. Grotta, J. Ranalli, M. S. Sokolikova, F. M. Pesci, P. Palczynski, V. L. Bemmer, and C. Mattevi, *ACS Omega* **3**, 8655 (2018).
- [28] C. Cong, J. Shang, X. Wu, B. Cao, N. Peimyoo, C. Qiu, L. Sun, and T. Yu, *Adv. Opt. Mater.* **2**, 131 (2013).
- [29] A. Ikeda, Y. Krockenberger, H. Irie, M. Naito, and H. Yamamoto, *Appl. Phys. Express* **9**, 061101 (2016).
- [30] Z. Luo, X. Lin, L. Tang, Y. Feng, Y. Gui, J. Zhu, W. Yang, D. Li, L. Zhou, and L. Fu, *ACS Appl. Mater. Interfaces* **12**, 34755 (2020).
- [31] C. Dai, B. Li, J. Li, B. Zhao, R. Wu, H. Ma, and X. Duan, *Nano Res.* **13**, 2506 (2020).
- [32] S. Liu, D. Li, G. Zhang, D. Sun, J. Zhou, and H. Song, *ACS Appl. Mater. Interfaces* **10**, 34193 (2018).
- [33] I. A. Solov'yov, A. V. Yakubovich, P. V. Nikolaev, I. Volkovets, and A. V. Solov'yov, *J. Comput. Chem.* **33**, 2412 (2012).
- [34] G. B. Sushko, I. A. Solov'yov, and A. V. Solov'yov, *J. Mol. Graph. Model.* **88**, 247 (2019).
- [35] M. Lu, Q. Yao, C. Xiao, C. Huang, and E. Kan, *ACS Omega* **4**, 5714 (2019).
- [36] A. A. Kistanov, S. A. Shcherbinin, R. Botella, A. Davletshin, and W. Cao, *J. Phys. Chem. Lett.* **13**, 2165 (2022).
- [37] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [38] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, *J. Phys.: Condens. Matter* **29**, 465901 (2017).
- [39] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [40] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [41] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [42] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010).
- [43] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [44] M. Methfessel and A. T. Paxton, *Phys. Rev. B* **40**, 3616 (1989).
- [45] I. A. Solov'yov, A. V. Korol, and A. V. Solov'yov, *Multi-scale Modeling of Complex Molecular Structure and Dynamics with MBN Explorer* (Springer International Publishing, Cham, Switzerland, 2017).
- [46] I. A. Solov'yov, A. V. Verkhovtsev, A. V. Korol, and A. V. Solov'yov, eds., *Dynamics of Systems on the Nanoscale* (Springer International Publishing, Cham, Switzerland, 2022).
- [47] A. V. Verkhovtsev, S. Schramm, and A. V. Solov'yov, *Eur. Phys. J. D* **68**, 246 (2014).
- [48] G. B. Sushko, A. V. Verkhovtsev, and A. V. Solov'yov, *J. Phys. Chem. A* **118**, 8426 (2014).
- [49] G. B. Sushko, I. A. Solov'yov, and A. V. Solov'yov, *Eur. Phys. J. D* **70**, 217 (2016).
- [50] P. de Vera, M. Azzolini, G. Sushko, I. Abril, R. Garcia-Molina, M. Dapor, I. A. Solov'yov, and A. V. Solov'yov, *Sci. Rep.* **10**, 20827 (2020).
- [51] J. Geng, I. A. Solov'yov, W. Zhou, A. V. Solov'yov, and B. F. G. Johnson, *J. Phys. Chem. C* **113**, 6390 (2009).
- [52] P. Moskovkin, M. Panshenskov, S. Lucas, and A. V. Solov'yov, *Phys. Stat. Sol. B* **251**, 1456 (2014).
- [53] K. Atkinson, R. Grimes, and S. Owens, *Solid State Ionics* **150**, 443 (2002).
- [54] M. Wilson, F. Hutchinson, and P. A. Madden, *Phys. Rev. B* **65**, 094109 (2002).
- [55] F. Hutchinson, M. K. Walters, A. J. Rowley, and P. A. Madden, *J. Chem. Phys.* **110**, 5821 (1999).
- [56] M. Matsui and M. Akaogi, *Molec. Simul.* **6**, 239 (1991).
- [57] A. Mattoni, A. Filippetti, M. I. Saba, and P. Delugas, *J. Phys. Chem. C* **119**, 17421 (2015).
- [58] L. M. Morgan, M. Molinari, A. Corrias, and D. C. Sayle, *ACS Appl. Mater. Interfaces* **10**, 32510 (2018).
- [59] A. Pedone, M. Bertani, L. Brugnoli, and A. Pallini, *J. Non-Cryst. Solids: X* **15**, 100115 (2022).
- [60] J. A. Nelder and R. Mead, *Comput. J.* **7**, 308 (1965).
- [61] F. Gao and L. Han, *Comput. Optim. Appl.* **51**, 259 (2012).
- [62] P. Li, L. F. Song, and K. M. Merz, Jr., *J. Phys. Chem. B* **119**, 883 (2015).
- [63] A. Turupcu, J. Tirado-Rives, and W. L. Jorgensen, *J. Chem. Theory Comput.* **16**, 7184 (2020).
- [64] P. Li and K. M. Merz Jr., *Chem. Rev.* **117**, 1564 (2017).
- [65] E. A. Mason, H. O'Hara, and F. J. Smith, *J. Phys. B: At. Mol. Phys.* **5**, 169 (1972).
- [66] D. Nelson, M. Benhenni, M. Yousfi, and O. Eichwald, *J. Phys. D: Appl. Phys.* **34**, 3247 (2001).
- [67] C. R. A. Catlow, M. Dixon, and W. C. Mackrodt, in *Computer Simulation of Solids. Lecture Notes in Physics*,

- vol. 166*, edited by C. R. A. Catlow and W. C. Mackrodt (Springer, Berlin, Heidelberg, 1982) pp. 130–161.
- [68] M. J. Gillan, J. Phys. C: Solid State Phys. **19**, 3391 (1986).
 - [69] B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990).
 - [70] S. Sundararaman, L. Huang, S. Ispas, and W. Kob, J. Chem. Phys. **148**, 194504 (2018).
 - [71] P. Ewald, Ann. Phys. **369**, 253 (1921).
 - [72] I. A. Solov'yov, G. Sushko, and A. V. Solov'yov, *MBN Explorer User's Guide (Version 3.0)* (MesoBioNano Science Publishing, Frankfurt am Main, 2017).
 - [73] H. Liu, Y. Li, Z. Fu, K. Li, and M. Bauchy, J. Chem. Phys. **152**, 051101 (2020).
 - [74] L. V. Woodcock, C. A. Angell, and P. Cheeseman, J. Chem. Phys. **65**, 1565 (1976).
 - [75] G. J. Kramer, N. P. Farragher, B. W. H. van Beest, and R. A. van Santen, Phys. Rev. B **43**, 5068 (1991).
 - [76] S. Alnemrat and W. W. Tomlinson, J. Magn. Magn. Mater. **566**, 170317 (2023).
 - [77] A. V. Verkhovtsev, M. Hanauske, A. V. Yakubovich, and A. V. Solov'yov, Comput. Mater. Sci. **76**, 80 (2013).
 - [78] A. Kochaev, Phys. Rev. B. **96**, 155428 (2017).
 - [79] K. Liu and J. Wu, J. Mater. Res. **31**, 832 (2015).
 - [80] B. Zhang, L. Zhang, N. Yang, X. Zhao, C. Chen, Y. Cheng, I. Rasheed, L. Ma, and J. Zhang, J. Phys. Chem. C **126**, 1094 (2022).
 - [81] C. Lee, X. Wei, J. W. Kysar, and J. Hone, Science **321**, 385 (2008).
 - [82] K. Liu, Q. Yan, M. Chen, W. Fan, Y. Sun, J. Suh, D. Fu, S. Lee, J. Zhou, S. Tongay, J. Ji, J. B. Neaton, and J. Wu, Nano Lett. **14**, 5097 (2014).
 - [83] D. S. Lide, ed., *CRC Handbook of Chemistry and Physics*, 84th ed. (CRC Press, Boca Raton, 2003).
 - [84] B. Luo, Y. Yao, E. Tian, H. Song, X. Wang, G. Li, K. Xi, B. Li, H. Song, and L. Li, Proc. Natl. Acad. Sci. U.S.A. **116**, 17213 (2019).