

Stable Compound of Helium and Sodium at High Pressure

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Helium, on par with neon, is the most chemically inert element in the Periodic Table. Due to its extremely stable closed-shell electronic configuration with record-high ionization potential and nearly zero electron affinity, helium is not known to form thermodynamically stable compounds (with the exception of inclusion compounds with weak van der Waals bonding). Here, using ab initio evolutionary algorithm USPEX, we predict the existence of a thermodynamically stable compound of helium and sodium, Na_2He with a fluorite-type structure, and this compound is predicted to be stable at pressures of > 160 GPa, well below the pressures required for compounds of He with other elements. In this novel electride phase, we consider electron pairs, localized in interstices, as special anions that have their own radii and volumes. The stability of this surprising phase is rationalized in terms of Pauling's rules, by analysis of charge density distribution and the electronic structure. Moreover, important roles are played by partial occupation of p -orbitals of He and increasing reactivity of Na at high pressure.

Helium (He) is the second most abundant element in the universe, after hydrogen, and plays an enormous role in normal stars and gas giant planets, such as Jupiter and Saturn [1]. It is, on par with neon, the most inert element in the Periodic Table, with no known stable compounds with other elements at any conditions. This is easy to understand as the ionization potential of the helium atom (24.59 eV [2]) is the highest among all elements, and its electron affinity (0.080 eV [3]) is close to zero. In the last decades, many scientists tried to find stable compounds of helium. The most successful example is the HHe^+ radical [4], which is only stable as a charged molecule and is an extremely aggressive chemical, protonating any base. All neutral molecules that have been found in theory or experiment, for example HHeF [5], $(\text{HeO})(\text{CsF})$ [6], and LiHe [7], are metastable and have a very high energy. For instance, HHeF has energy of more than 2 eV/atom higher than the mixture of HF molecules and He atoms. The only known stable solid compounds involving helium are van der Waals compounds, such as NeHe_2 [8]. Such compounds are formed at elevated pressures and are characterized by ultradense packing (e.g. Laves-phase structures) that give them advantage under pressure.

Pressure greatly affects chemical properties of the elements. Recent theoretical investigation [9] found that pressure increases the reactivity of xenon and its oxides become thermodynamically stable at experimentally reachable pressures (> 83 GPa). It was also found that high pressure will cause strong interstitial electron localization in alkali and alkaline-earth elements [10, 11]. Particularly, sodium becomes an insulator due to strong core-core orbital overlap leading to interstitial valence electron localization. Furthermore, under pressure, unexpected compounds, such as Na_3Cl , Na_2Cl , Na_3Cl_2 , NaCl_3 and NaCl_7 [12], Mg_3O_2 and MgO_2 [11], become stable. Using large-scale computations utilizing variable-composition evolutionary structure prediction, we explored the possibility of formation of stable compounds of helium with a variety of elements (H, O, F, Na, K, Mg, Li, Rb, Cs, etc), and to our great surprise we found that only Na readily forms a stable compound with He at rather moderate pressures. Below we focus on results for the He-Na system.

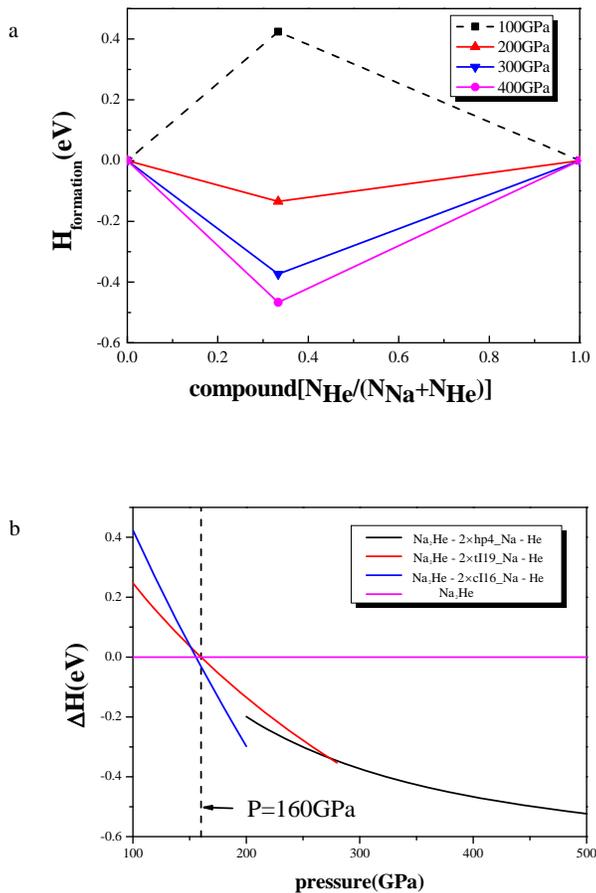


FIG. 1. a. Predicted formation enthalpy of compound in the Na-He system at pressures of 100, 200, 300 and 400 GPa. For He, the hexagonal close-packed (hcp) structure [13] was used in the calculations. For Na, cI16 [14] at 100 GPa, tI19 [15] at 200 GPa, hP4 [10] at 300 and 400 GPa, were used. b. Enthalpy of formation as a function of pressure. Our calculated pressure of Na transformation from the cI16 to the tI19 structure is 151 GPa, and from tI19 to hP4 it is 273 GPa, similar to previous calculations [10].

The Na-He system was studied using variable-composition evolutionary structure prediction algorithm [16, 17] as imple-

mented in the USPEX code [18, 19]. In such calculations, a phase is deemed stable if its enthalpy of formation from the elements or any other possible compounds is negative. Variable-composition structure searches were performed for the Na-He system at pressures of 0, 150, 200, 400, 700 and 1000 GPa, allowing up to 36 atoms per cell. Unexpectedly, we found a new compound Na₂He (Fig. 2a) which has lower enthalpy than the mixture of elemental Na and He, or any other mixture, at pressures above 160 GPa (Fig. 1b). The reaction



has negative enthalpy of formation at pressures above 160 GPa, which increases in absolute value on increasing pressure and reaches a large value of -0.51 eV per formula unit at 500 GPa. We also performed quasiharmonic free energy calculations based on the computed phonon spectra to consider the effect of temperature on Gibbs free energy. The free energy of formation changes little with temperature - for example, at the pressure of 300 GPa, when the zero-point energy is included, it increases from -0.41 eV at 0 K to -0.39 eV at 800 K (Fig. S2). Phonon calculations also clearly indicate the dynamical stability of this structure above 100 GPa (Fig. S1). This means that, once formed at pressures above 160 GPa, this phase can be decompressed down to 100 GPa (but already by 50 GPa it becomes dynamically unstable and is therefore unquenchable to ambient conditions).

Note that Na₂He becomes stable at the pressure close to that of transition of Na from the cI16 to the tI19 structure. The transition in Na has an underlying electronic stabilization mechanism related to the development of a pseudogap or gap in the electronic density of states at the Fermi energy (tI19 is a very poor metal, and hP4, the phase appearing on further increase of pressure, is a wide-gap insulator [10]). This hints at a possible stabilization of Na₂He due to electronic effects. Indeed, Na₂He has a surprisingly wide band gap in the entire pressure range of its stability.

Na₂He has only one ground-state structure in the whole pressure range explored here, i.e. from 160 GPa to 1000 GPa. It belongs to the structure type of fluorite (CaF₂) and has cubic space group $Fm\bar{3}m$ with Na atoms occupying the Wyckoff positions 8c(0.25,0.25,0.25) and He atoms occupying the 4a(0,0,0) positions. The lattice parameter is $a = b = c = 3.95\text{\AA}$ at 300 GPa. He atoms are in an eightfold (cubic) coordination, and Na atoms have a fourfold (tetrahedral) coordination. Fig. 2a and Fig. 2b show this structure in the conventional and primitive cells, respectively.

An intriguing question is the cause of stability of such a strange compound; it could be expected that helium would more readily form stable compounds with the most electronegative atoms, especially fluorine (analogous to xenon, which forms stable fluorides at ambient conditions, and stable oxides under pressure [9]), but our calculations show that helium fluorides are not thermodynamically stable even at the extremely high pressures above 800 GPa, which can be traced to helium's extremely high ionization potential (24.59 eV), the highest in the Periodic Table. The formation of a stable compound with an electropositive atom, such as sodium, is at first puzzling - helium has a nearly zero electron affinity of 0.08 eV, making it unlikely to play the role of an anion, even with alkali atoms.

To reveal the origin of this unexpected Na-He compound, we analyzed its electronic structure and chemical bonding using electron localization function (ELF) [20] and deformation charge density distribution [21]. Both analyses reveal strong interstitial electron localization in the structure of Na₂He (Fig. 2b, Fig. 2c), similar to hP4-Na. The localized electrons occupy the Wyckoff 4b(0.5,0.5,0.5) positions, i.e. are in the middle of cell edges and in the center of the cubic cell. Just like hP4-Na [10], Na₂He can be described as an electride, i.e. ionic crystal where the role of an anion is played by a localized electron. If we suppose that Na ions have +1 net charge and He atoms are neutral, given that the number of sodium atoms is twice the number of electron localizations, one concludes that the localized electron is actually an electron pair. Similarly, transparent high-pressure form of sodium, hP4-Na [10], also has 4 Na atoms and 2 localized electron pairs in the unit cell. One can write the structural formula of Na₂He as Na₂He(2e⁻). Na₂He and hP4-Na differ fundamentally from the known low-pressure electrides (Dye, 2003 [22]), where interstitially localized electrons are unpaired and spin-polarized. Spin pairing increases the density, making electron-paired electrides stable under pressure; the same explanation is valid for the high spin - low spin transitions in d-elements under pressure. Spin pairing in compressed electrides is a new phenomenon.

Localized electron pairs, together with the Na and He atoms, create a structure, derivative of the AlCu₂Mn type: in the structure of AlCu₂Mn (Na₂He2e⁻), atoms of Al (He) form a cubic close packing (face-center cubic packing), all tetrahedral voids in which are filled by the Cu (Na) atoms, and all octahedral voids are filled by the Mn atoms (electron pairs, 2e⁻). This structure is closely related to the Fe₃Al structure type and Heusler alloys X₂YZ, which can be very dense. In this structure, every Na atom is surrounded by 4 He atoms and 4 localized electron pairs, and every He atom or localized electron pair is coordinated by 8 Na atoms. This description is more justified than the naive view ignoring interstitial electron pairs and classifying this material as fluorite-type. Indeed, the fluorite structure is not dense and in all known compounds becomes unstable already at moderate pressures [23].

Analysis of the band structure further supports the analogy between Na₂He and hP4-Na. Na₂He turns out to be a wide-gap insulator. This is surprising: according to the Wilson model [24], the insulator-metal transition should occur under pressure due to the expected widening of the valence and conduction bands on compression, leading to gap closure under pressure. However, both hP4-Na and Na₂He display the reverse behavior: these high-pressure phases are insulating in their entire stability fields,

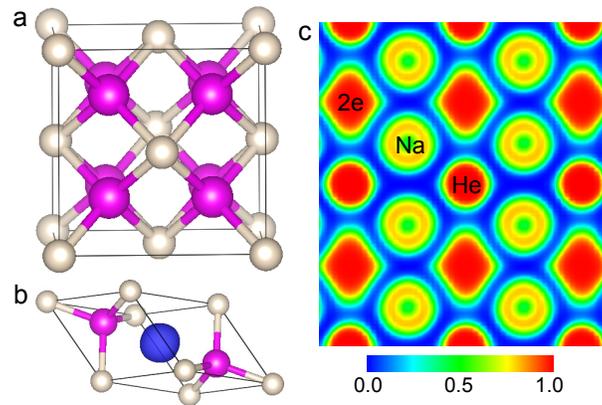


FIG. 2. Crystal structure of Na_2He at 300 GPa: (a) conventional cell, (b) primitive cell. Pink atoms represent Na and white atoms represent He. Panel (b) shows deformation charge density (i.e. crystal density minus the sum of isolated atomic densities) of Na_2He with an isosurface of $0.03 \text{ e}\text{\AA}^{-3}$. (c) ELF plotted in the $[110]$ plane of conventional cell at 300 GPa.

and their band gaps increase under pressure. The band gaps of Na_2He and hP4-Na from GW calculations (well known to provide an accurate description of band gaps, to within 5-10% of experimental values [25]) are shown as a function of pressure in Fig. 3b. With direct band gaps exceeding 2.7 eV at pressures above 300 GPa, both Na_2He and hP4-Na are expected to be optically transparent; for hP4-Na, its prediction was experimentally confirmed [10]. It is noteworthy that Na_2He has a wider gap than hP4-Na at pressures below 230 GPa.

Interstitial localization of valence electrons is an important phenomenon that may occur in many systems at sufficient compression, and can be seen as a multicenter bond. At normal pressure, multicenter bonds manifest themselves as charge density "bridges" with delocalized orbitals, e.g. in aromatic systems or in metals. Under sufficiently high pressure, when atomic core regions overlap with core or valence electrons of neighboring atoms, valence orbitals are deformed (due to strong repulsion from the core electrons) and part of valence electron density is forced into the voids of the structure. This leads to valence band narrowing [26], opposite to band widening, commonly observed in normal systems and leading to the Wilson transition. For Na_2He , the shortest Na-He distance is 1.71 Å and the shortest Na-Na distance is 1.98 Å at 300 GPa. Recall that the outermost valence orbital radii of the Na and He atoms are 1.71 Å and 0.29 Å, respectively [27]. As the effective size of the core of Na atoms, one can take the radius of Na^+ ionic, 1.02 Å [28]. The Na-He distance (1.71 Å) is significantly shorter than the sum of the outermost orbital radii of Na and He (2.00 Å), and the Na-Na distance (1.98 Å) is slightly shorter than the sum of Na core radii (2.04 Å) and much shorter than the sum of valence and core radii of Na atoms (2.73 Å), implying strong Na-He and Na-Na core-valence overlap, and Na-Na core-core overlap leading to strong localization of valence electrons in Na_2He . Note that Na_2He becomes stable at a lower pressure than hP4-Na (theoretical transition pressures are 160 GPa and 273 GPa, respectively, and both numbers are likely to be overestimates due to well-known tendency of DFT calculations to underestimate stability fields of systems with localized electronic states).

Quantum mechanics can prove that interstitial electron pairs, once localized in space, are expected to prefer spherical shape to minimize their kinetic energy, as we see from our calculations (Fig. S3), and thus may be characterized by volumes and radii, as normal atoms, which reinforces the description of Na_2He as an electride. Note that in Na_2He the localized interstitial electron pairs have much higher symmetry than in hP4-Na ($m\bar{3}m$ vs $\bar{6}m2$) and is closer to sphericity.

We can bring the electride description one step further, considering it as a special kind of ionic crystal that satisfies basic rules for ionic structures, which explain why Na reacts with He, forming the stable compound Na_2He . Pauling's first rule [29] states that the cation-anion distance is determined by the sum of ionic radii and the coordination number is determined by the radius ratio. To get the radii under pressure, we performed Bader analysis [30, 31] at different pressures and obtained the radius as the shortest distance from an atom to its Bader boundary. Na atoms are the largest in this compound and we take them as reference, for convenience of defining radius ratios. The radii of He atoms and electron pairs to Na at 200 GPa are 0.852 and 0.772, respectively, and they decrease a little to 0.820 and 0.740, as pressure increases to 500 GPa. The decrease demonstrates that Na atoms are the least compressible at such high pressures, where ionic core is being compressed. Radius ratios greater than 0.732 imply that He atoms and electron pairs should have eightfold (cubic) coordination by Na atoms, which is exactly what we see in the structure. One can alternatively describe this structure as a CaF_2 -type structure formed by Na atoms and electron pairs, with nearly neutral He atoms filling interstitial positions. In this description, it is clearly seen that Na_2He also satisfies Pauling's second rule [29], i.e. local balance of bond valences. On the contrary, hP4-Na does not satisfy this rule, which explains why hP4-Na so readily reacts with He to form Na_2He . One can also note that Na_2He better fulfills the fifth Pauling's rule, i.e.

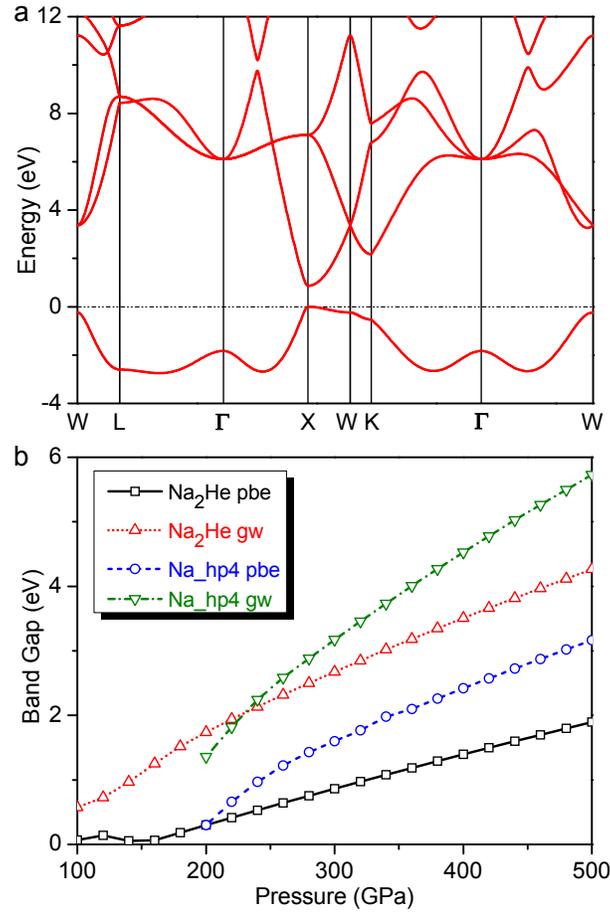


FIG. 3. Electronic structure of Na₂He: (a) band structure at 300 GPa, (b) band gaps (calculated by DFT and GW methods) for hp4-Na and Na₂He as a function of pressure. The results for hp4-Na agree well with those in [10].

TABLE I. Calculated Bader charges and radius ratios, relative to Na, at pressures of 200, 300 and 500 GPa. For comparison, we list Bader charges of hp4-Na.

Pressure (GPa)	hp4-Na		Na ₂ He		
	item	charge	item	charge	radius ratio
200	Na1	0.571	Na	0.599	1.000
	Na2	0.505	He	-0.174	0.852
	e	-1.076	2e ⁻	-1.022	0.772
300	Na1	0.603	Na	0.601	1.000
	Na2	0.508	He	-0.159	0.834
	e	-1.108	2e ⁻	-1.043	0.755
500	Na1	0.644	Na	0.612	1.000
	Na2	0.511	He	-0.146	0.820
	e	-1.155	2e ⁻	-1.079	0.740

minimum number of different building blocks and maximum symmetry.

Examining Bader charges (Table I), we see that the values for Na atoms in Na₂He are very similar with Na1 in hp4-Na, close to +0.6, and that He atoms have a small negative charge (~ -0.15 e), and the non-nuclear charge maximum contains slightly more than 1 electron (and this number increases in absolute value with pressure). Interestingly, upon the formation of Na₂He from hp4-Na and hcp-He, the greatest charge transfer (~ -0.15 e) occurs from Na2 atoms in hp4-Na to He in Na₂He. This charge transfer can be explained by much weaker repulsion of valence electrons from the small core of He atoms. Furthermore, He core does not contain *p*-orbitals and thus *p*-orbitals can be quite compact, due to the absence of orthogonality constraints. This

TABLE II. Bader volume difference analysis of Na₂He at 200 and 500 GPa. The data for the Na atom in Na₂He are relative to the Na1 and Na2 in Na-hP4, the data for the He atom are relative to hcp-He. Enthalpies and energies are given per formula.

	Na	He	e	total	$\Delta E(eV)$	$\Delta H(eV)$
200 GPa	$\Delta V(\text{\AA}^3)$	-0.28, -0.38	0.82 -0.54	-0.38	0.27	-0.20
	$P\Delta V(eV)$	-0.35, -0.48	1.03 -0.67	-0.47		
500 GPa	$\Delta V(\text{\AA}^3)$	-0.00, -0.24	0.46 -0.28	-0.07	-0.30	-0.51
	$P\Delta V(eV)$	-0.01, -0.76	1.43 -0.87	-0.21		

also contributes to stability of Na₂He relative to the elemental Na and He. This helps He to adopt negative charge and the extra electrons occupy the normally empty 2s and 2p orbitals, as we see in the projected densities of states (PDOS) in Fig. 4. The PDOS shows that He 2s,2p and Na 3s,3p,3d orbitals hybridize to form the valence band.

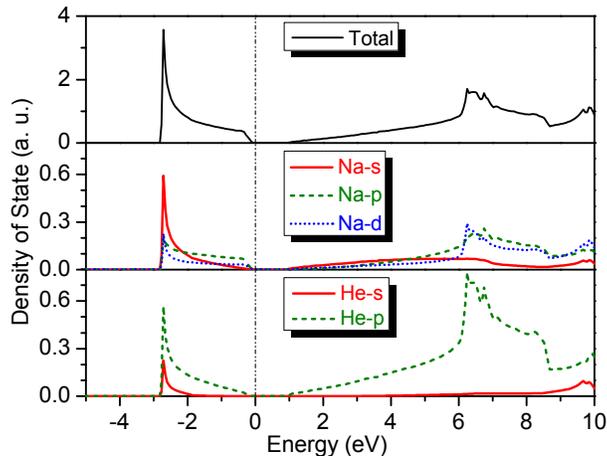


FIG. 4. Total and projected densities of states of Na₂He at 300 GPa. The Fermi energy is set as zero and shown by the dashed line.

Bader volume data (Table II) shows the same picture, but with interesting additional details. Atomic volume of He increases in Na₂He, due to its acquisition of a negative charge - the contributes to the PV-term in the formation enthalpy increasing from 1.03 eV at 200 GPa to 1.43 eV at 500 GPa, destabilizing the compound. However, this is more than compensated by the other entities - at 200 GPa, the combined PV-term of Na1 and Na2 atoms in the enthalpy of formation is -0.83 eV and localized electron pairs make a stabilizing contribution of -0.67 eV; at 500 GPa, the data change to -0.77eV and -0.87eV, respectively. Compactification of Na atoms and localized electron pairs are prime factors stabilizing Na₂He.

Na is a light alkali metal, and is less reactive than heavier K, Rb and Cs at ambient pressure. One could expect stable compounds in K-He, Rb-He and Cs-He systems at even lower pressures, but our calculations show that there are no thermodynamically stable compounds in these systems at pressures below 1000 GPa. However, for Li, we find that Li₂He₅ becomes stable at 780 GPa. This implies that light alkali metals (Li and Na) behave quite differently from the heavy ones (K, Rb and Cs). Just as discussed by Winzenick et al. [32], heavier alkali metal under pressure undergo an s→d electronic transition, making them "incipient transition metals". Let us take K as an example: K has electronic configuration [Ar]4s¹, which under pressure transforms into [Ar]3d¹, and the 3d-electron will be rather localized and able to penetrate the core. Rather than being lost or transferred to helium's 2s- or 2p-orbitals, this valence 3d-electron will be largely retained by the K atom, and there would be no compounds in the K-He system. Under pressure, Na will, paradoxically, have lower electronegativity and higher reactivity than K - because Na has electronic configuration [Ne]3s¹ and transferring the valence electron onto the nearest d-orbital (empty 3d-orbital) is energetically costly. It is the combined action of external pressure and interelectronic interactions that force valence electrons of the alkali metal onto the empty orbitals of the He atoms.

We can make a generalization for M-He systems. Na displays a rapid decrease of electronegativity with pressure, which makes it readily react with He. Counterintuitively (but in agreement with our calculations), due to the s→d electronic transition, heavier alkali metals (K, Rb, Cs) will have higher electronegativity than Na. Moreover, heavy alkali metals do not have strong interstitial electron localizations: the valence electron penetrates the core (again, due to the s→d transition) instead of being repelled and localized into the empty spaces of the structure. In its highly reactive electronegative state, Na reacts with He at rather low pressures, but none of this kind of phenomenon happens in heavy alkali metals at least below 1000 GPa. For Li, high-pressure reactivity is

below that of Na (just as at normal conditions), but greater than for the "incipient d metals" (K, Rb and Cs), so the situation is intermediate, and a stable compound Li_2He_5 is found above 780 GPa.

In conclusion, systematic search for stable compounds of helium has, unexpectedly, resulted in the prediction of a cubic phase Na_2He , stable from 160 GPa up to at least 1000 GPa. This phase is an electride, i.e. a crystal made of positively charged ionic cores and strongly localized valence electrons playing the role of anions. Its stability is explained by Pauling's rules and analysis of the electronic structure. Compared with similar electride hP4-Na, the participation of He atoms brings high symmetry, weak repulsion of the valence electrons from He core, and hybridization of the valence orbitals of He and Na atoms. Pauling's rules are perfectly satisfied for Na_2He , but not for hP4-Na, explaining why Na and He so readily react under pressure and Na_2He is so stable. This is the first reported thermodynamically stable compound of He with strong chemical bonding, giving start to the hitherto empty field of helium chemistry and giving new twists to the chemistry of noble gases, which will have impact on our understanding of chemical bonding and chemical processes that occur inside giant planets.

METHODS

The evolutionary algorithm USPEX [18, 19], used here for predicting new stable structures, searches for the structure with the lowest enthalpy at specific pressure and is available to predict the stable structure of a compound knowing just the chemical composition. A number of applications [10, 19, 33] illustrate its power. Structure relaxations were performed using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) functional [34] in the framework of the all-electron projector augmented wave (PAW) method [35] as implemented in the VASP code [36]. The PAW pseudopotentials were used of $2s^22p^63s$ electrons treated as valence with 1.2 a.u. core radius for Na and $1s^2$ electrons treated as valence with 1.1 a.u. core radius for He. We used a plane-wave kinetic energy cutoff of 900 eV, and the Brillouin zone was sampled with a resolution of $2\pi \times 0.06\text{\AA}^{-1}$, which showed excellent convergence of the energy differences, stress tensors and structural parameters. The first generation of structures was created randomly. All structures were relaxed at constant pressure and 0 K and the enthalpy was used as fitness. The energetically worst structures (40%) were discarded and a new generation was created 30% randomly and 70% from the remaining structures through heredity, lattice mutation and permutation of atoms. For property calculation, such as enthalpy, Bader charge and bandstructure, we used kinetic energy cutoff of 1000 eV and sampling the Brillouin zone with $2\pi \times 0.03\text{\AA}^{-1}$. We explored the effects of temperature using the quasiharmonic approximation, for which phonon calculations were performed for all promising structures using the PHONOPY code [37] with the Density-Functional Perturbation Theory (DFPT) method; for each structure, phonons were computed at 20 different volumes to predict the Gibbs free energy.

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- [1] D. J. Stevenson, Proc. Natl. Acad. Sci. **105**, 11035 (2008).
- [2] J. E. Huheey, E. A. Keiter, R. L. Keiter, and O. K. Medhi, *Inorganic chemistry: principles of structure and reactivity* (Harper & Row New York, 1983).
- [3] B. Brehm, M. A. Gusinow, and J. L. Hall, Phys. Rev. Lett. **19**, 737 (1967).
- [4] J. W. Hiby, Annalen der Physik **426**, 473 (1939).
- [5] M. W. Wong, J. Am. Chem. Soc **122**, 6289 (2000).
- [6] W. Grochala, Pol. J. Chem. **83**, 87 (2009).
- [7] N. Tariq, N. Taisan, V. Singh, and J. D. Weinstein, Phys. Rev. Lett. **110**, 153201 (2013).
- [8] P. Loubeyre, M. Jean-Louis, R. LeToullec, and L. Charon-Gérard, Phys. Rev. Lett. **70**, 178 (1993).
- [9] Q. Zhu, D. Y. Jung, A. R. Oganov, C. W. Glass, C. Gatti, and A. O. Lyakhov, Nat. Chem. **5**, 61 (2012).
- [10] Y. Ma, M. Eremets, A. R. Oganov, Y. Xie, I. Trojan, S. Medvedev, A. O. Lyakhov, M. Valle, and V. Prakapenka, Nature **458**, 182 (2009).
- [11] Q. Zhu, A. R. Oganov, and A. O. Lyakhov, Phys. Chem. Chem. Phys. (2013).
- [12] W. Zhang, A. R. Oganov, A. F. Goncharov, Q. Zhu, S. E. Boulfelfel, A. O. Lyakhov, M. Somayazulu, and V. B. Prakapenka, arXiv preprint arXiv:1211.3644 (2012).
- [13] J. M. McMahon, M. A. Morales, C. Pierleoni, and D. M. Ceperley, Rev. Mod. Phys. **84**, 1607 (2012).
- [14] E. Gregoryanz, O. Degtyareva, M. Somayazulu, R. J. Hemley, and H.-k. Mao, Phys. Rev. Lett. **94**, 185502 (2005).
- [15] E. Gregoryanz, L. F. Lundegaard, M. I. McMahon, C. Guillaume, R. J. Nelmes, and M. Mezouar, Science **320**, 1054 (2008).
- [16] A. O. Lyakhov, A. R. Oganov, and M. Valle, Modern Methods of Crystal Structure Prediction(ed. A.R. Oganov), 147 (2010).
- [17] A. R. Oganov, Y. Ma, A. O. Lyakhov, M. Valle, and C. Gatti, Rev. Mineral. Geochem. **71**, 271 (2010).
- [18] A. R. Oganov and C. W. Glass, J. Chem. Phys. **124**, 244704 (2006).
- [19] C. W. Glass, A. R. Oganov, and N. Hansen, Comput. Phys. Commun. **175**, 713 (2006).
- [20] A. D. Becke and K. E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990).
- [21] F. Hirshfeld, Theoretica Chimica Acta **44**, 129 (1977).

- [22] J. L. Dye, *Science* **301**, 607 (2003).
- [23] L. Gerward, J. S. Olsen, S. Steenstrup, M. Malinowski, S. Asbrink, and A. Waskowska, *J. Appl. Crystallogr.* **25**, 578 (1992).
- [24] N. Mott and Z. Zinamon, *Reports on Progress in Physics* **33**, 881 (1970).
- [25] M. Shishkin and G. Kresse, *Phys. Rev. B* **75**, 235102 (2007).
- [26] B. Rousseau and N. W. Ashcroft, *Phys. Rev. Lett.* **101**, 046407 (2008).
- [27] J. Waber and D. T. Cromer, *J. Chem. Phys.* **42**, 4116 (1965).
- [28] R. t. Shannon and C. T. Prewitt, *Acta Cryst. B* **25**, 925 (1969).
- [29] L. Pauling, *J. Am. Chem. Soc* **51**, 1010 (1929).
- [30] R. F. Bader, *Atoms in molecules* (Wiley Online Library, 1990).
- [31] G. Henkelman, A. Arnaldsson, and H. Jónsson, *Comput. Mat. Sci.* **36**, 354 (2006).
- [32] M. Winzenick, V. Vijayakumar, and W. B. Holzapfel, *Phys. Rev. B* **50**, 12381 (1994).
- [33] A. R. Oganov, J. Chen, C. Gatti, Y. Ma, Y. Ma, C. W. Glass, Z. Liu, T. Yu, O. O. Kurakevych, and V. L. Solozhenko, *Nature* **457**, 863 (2009).
- [34] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [35] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [36] G. Kresse and J. Furthmüller, *Comput. Mat. Sci.* **6**, 15 (1996).
- [37] A. Togo, F. Oba, and I. Tanaka, *Phys. rev. B* **78**, 134106 (2008).

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