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SODIUM CHLORIDE PHASES

2D materials worth their salt

Sodium chloride phases with unconventional non-1:1 stoichiometries are known to exist under high-pressure conditions. Now, Na_2Cl and Na_3Cl two-dimensional crystals have been obtained under ambient conditions, on graphene surfaces, from dilute solutions.

Artem R. Oganov

It was in the early nineteenth century that John Dalton proposed the law of multiple proportions, which characterized the proportions of different elements present in compounds in terms of atomic ratios, underpinning stoichiometry. It has since been revisited with the notion of valence: if atoms A and B with (integer) valences m and n , respectively, form a stable compound, then the expected formula of this compound will be A_nB_m . This nicely explains why sodium chloride is NaCl — and this archetypal ionic compound has long been known for its reliable 1:1 stoichiometry. We know that owing to the large difference in their electronegativity Na and Cl will form highly ionic bonds, and under ambient conditions NaCl crystallizes in the ‘rocksalt’ structure (a face-centred cubic lattice that consists of alternating cations and anions). Now, as described in *Nature Chemistry*, in addition to films of this ‘normal’ rocksalt NaCl Haiping Fang, Minghong Wu and co-workers have experimentally grown thin films of Na_2Cl and Na_3Cl on graphene-based substrates (Fig. 1)¹. It is particularly intriguing that these chemically unintuitive stoichiometries arise under ambient conditions.

Recently, the ‘well-behaved’, seemingly well-understood Na–Cl and K–Cl systems have been shown to adopt a variety of unconventional (non-1:1) stoichiometries under high pressures^{2,3}. The phases described include Na_3Cl , NaCl_3 and KCl_3 , which were predicted by quantum-mechanical simulations and then synthesized in a laser-heated diamond anvil cell, as well as many others such as Na_2Cl , Na_3Cl_2 , NaCl_7 , K_3Cl , K_2Cl , K_3Cl_2 , K_5Cl_4 , K_3Cl_5 and KCl_7 , which have been

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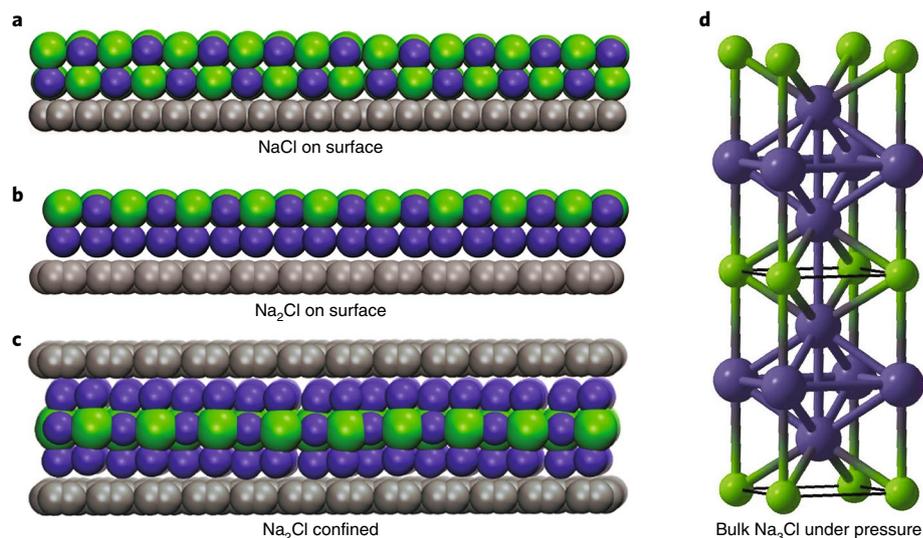


Fig. 1 | Structures of sodium chloride phases with unconventional stoichiometries. **a**, NaCl on graphene. **b**, Na_2Cl on graphene. **c**, Na_3Cl sandwiched between two graphene sheets. **d**, Bulk Na_3Cl obtained under high pressure⁷. This phase shows alternate Na and NaCl layers, as do the two-layer Na_2Cl and three-layer Na_3Cl materials epitaxially grown in the present work. Colour code: Purple, Na; green, Cl; grey, C. Panels **a–c** are reproduced from ref. ¹, Macmillan Publishers Ltd; panel **d** is adapted from ref. ², AAAS.

predicted but not (yet) experimentally tried. Such a departure from the familiar 1:1 stoichiometry is noteworthy, and it seems likely that at sufficiently high pressures such exotic phases will appear in all chemical systems. They may well play a very important role in planetary interiors, where high pressures reign. For example, the decomposition of FeOOH (rust) into FeO_2 — with H_2 release — under pressure and temperature conditions relevant to the Earth’s deep lower mantle, was recently

explored⁴. Exotic stoichiometries may also give rise to exciting properties. One such surprising compound, H_3S , was predicted⁵ to be the highest-temperature superconductor — and then synthesized and experimentally shown⁶ to exhibit superconductivity at 203 K and 155 GPa.

The reason these phases arise under pressure is not well understood. Many of these compounds with unconventional stoichiometries are metallic, prompting one to excuse their existence as we

notoriously cannot explain stoichiometries of intermetallides. Yet many others of these exotic compounds are semiconducting, and for these, classical explanations should work better.

In the present work, the fact that Na_2Cl and Na_3Cl have been grown under ambient pressure using another form of extreme condition — surfaces — is exciting. In fact, it is known that crystal surfaces can have well-defined stoichiometries that are different from those of the bulk, and these are determined by external conditions (such as the chemical potentials of the crystals' components in the surrounding solution during growth), but the epitaxial growth of such unusual phases had not been noticed. By immersing different substrates in undersaturated solutions of sodium chloride, the researchers successfully prepared NaCl films on graphene (Fig. 1a), thin films of Na_2Cl on graphene (Fig. 1b) and on reduced graphene oxide substrates, and thin films of Na_3Cl sandwiched between two graphene sheets (Fig. 1c)¹. The resulting 2D materials were then dried, their atomic structures characterized by X-ray diffraction, and the ratios of Na to Cl were determined by energy-dispersive X-ray spectroscopy.

Because the characterization of these 2D materials is extremely complicated, some caution should be exercised; for example, different epitaxial phases were distinguished by just one X-ray reflection (which only subtly varies from NaCl to Na_2Cl to Na_3Cl). The surface-induced 2D crystals are also shown to have Na:Cl ratios varying from 0.2 to 6. Very few measurements correspond to Na:Cl < 1 and > 3, many correspond to Na:Cl = 1 as should be expected and, notably, a large number of data are found with Na:Cl ratios between 1 and 3. The data at hand points to the presence of Na_2Cl and Na_3Cl phases, as described by Fang, Wu and co-workers, though the uncertainties seem to be too large for one to be fully confident in the exact compositions, inviting future characterization work. In any case, the fact that phases with unusual stoichiometries were grown under ambient conditions is undeniable, and those materials' structures are certainly intriguing.

The researchers also note¹ that similar behaviour was found also for other

chloride solutions, such as KCl solutions, although they have not yet reported the stoichiometries of the resulting 2D crystals. The fact that such a disarmingly simple experiment is sufficient for creating compounds long thought to be impossible is in itself exciting, and may have consequences for the generation of unusual phases, perhaps with unusual properties.

Molecular dynamics and density functional theory were also carried out to investigate the crystallization process. They suggest that it is driven by ion- π interactions between the Na^+ and/or Cl^- centres and the substrates' aromatic rings, which in turn promote the adsorption of the ions on the surface. A stronger ion- π interaction with sodium compared to chloride would account for the higher proportion of sodium atoms in the resulting materials.

Both the Na_2Cl and Na_3Cl phases are described by Fang, Wu and co-workers as comprising a pure sodium layer first grown on the graphene substrate with a NaCl layer above it (Fig. 1b) then, in the case of Na_3Cl sandwiched between two graphene sheets, another pure sodium layer before the second graphene layer (Fig. 1c). This is reminiscent of the structure observed for the high-pressure Na_3Cl bulk phase (Fig. 1d), which consists of alternate Na and NaCl layers², and which incidentally was shown to be a 2D metal. Here, by analogy, in the Na_3Cl crystal on graphene we may expect electronic conduction within the layer of sodium atoms. Such metallic interface layers can be expected in other epitaxial phases, and they may offer a route to the miniaturization of electronic devices down to the atomic scale. New physics may emerge too, as in the case of superconductivity at the $\text{LaTiO}_3/\text{SrTiO}_3$ interface⁷.

Because sodium has low resistance to shear (as shown for example by its very low elastic constants⁸), the pure sodium layer on top of the graphene substrate may also reduce friction on the overall material. This points to a possible practical use of stoichiometry tuning in epitaxially grown phases, if it could be controlled. Notably, another unexpected 2D crystal was recently observed sandwiched between two graphene sheets: 'square ice'⁹, in which water molecules adopt a hydrogen-bonding geometry that is

puzzling given the hexagonal symmetry of both graphene and 'normal' ice.

Another interesting aspect is that the growth of these unexpected epitaxial phases, formed here in undersaturated solutions, may reflect the early stages of epitaxial crystal growth more generally. Can it be that phases of unusual stoichiometries first appear and, after a few atomic layers, the 'normal' compounds grow? The observation of these exotic phases makes this scenario plausible.

Many exciting questions and opportunities arise from these findings. What stabilizes these epitaxial compounds and what determines their stoichiometries? The researchers state that the extra layer of sodium atoms on top of graphene donates electrons to the π -bonding system of graphene¹. Is it a coincidence that the same stoichiometries (Na_2Cl and Na_3Cl) form both on graphene surfaces and in high-pressure bulk phases²? Are other stoichiometries and structures of sodium chlorides possible on graphene? Which epitaxial phases would form on other substrates? Further work will clarify these questions and, highly likely uncover new ones. What is clear from this work though is that the surfaces of materials — something seemingly mundane, which we constantly interact with — are far from being well understood and promote intriguing phenomena that are worthy of in-depth investigations. □

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