



Cite this: *J. Mater. Chem. C*, 2020, **8**, 10551

Received 5th March 2020,  
Accepted 14th April 2020

DOI: 10.1039/d0tc01165g

rsc.li/materials-c

## Electrides: a review

Chang Liu, <sup>a</sup> Sergey A. Nikolaev, <sup>b</sup> Wei Ren <sup>ac</sup> and Lee A. Burton <sup>\*a</sup>

Electrides are systems in which an electron is not bound to an atom and plays an active role in the materials structure. We present concise summaries of the different types of electride in the literature, in which we systematically revisit their history and discuss their unique behaviour. We go on to offer intuitive guidelines for novel electride discovery and suggest advice for the accurate treatment of their physical properties. In the end, we conclude on the common nature of all electrides, with an alternative definition intended to minimise confusion surrounding these materials.

## 1 Introduction

A material is usually considered to be either covalent or ionic depending on whether the valence electrons of atoms are shared (covalently bonded) or transferred (ionically bonded) between the constituent atoms.

Electrides are solids in which the electrons detach themselves entirely from their original atoms, as with the ionic case,

but do not fully transfer to a destination atom. The extra electron(s) remain within the material usually occupying interstitial space between cations, which has led to them being considered as anions. The anionic electrons, being not bound to a nucleus, are relatively free to diffuse, leading to high conductivities, and relatively easy to extract, leading to low work functions. Such properties allow for almost ideal application to various technologies including electron emitters,<sup>1</sup> superconductors,<sup>2</sup> battery anodes,<sup>3</sup> optics,<sup>4,5</sup> lamps,<sup>6</sup> radioactive waste storage,<sup>7</sup> and catalysts for a range of applications including organic synthesis,<sup>8</sup> ammonia production,<sup>9</sup> and CO<sub>2</sub> splitting.<sup>10</sup>

The anionic electron itself is not easy to identify, especially using the routine methods for crystal characterisation. Modern computational methods, such as density functional theory (DFT), allow for relatively accurate prediction of electronic

<sup>a</sup> International Centre for Quantum and Molecular Structures, Department of Physics, Shanghai University, Shanghai 200444, China. E-mail: leeburton@shu.edu.cn; Fax: +86 21 66134208; Tel: +86 21 66136129

<sup>b</sup> Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan. E-mail: nikolaev.s.aa@m.titech.ac.jp

<sup>c</sup> Materials Genome Institute and Shanghai Key Laboratory of High Temperature Superconductors, Shanghai University, Shanghai 200444, China. E-mail: renwei@shu.edu.cn



Chang Liu

Chang Liu received his BS degree from Fuyang Normal University in 2016. He is currently pursuing a PhD at the International Centre for Quantum and Molecular Structures, Shanghai University under the supervision of Prof. Wei Ren. His research direction is the design of Ferroelectrics, Multiferroics and Spin-electronics by first principle calculations.



Sergey A. Nikolaev

Dr Sergey A. Nikolaev received his PhD in condensed matter physics from the Ural Federal University in Russia and now works as a specially appointed Assistant Professor at the Tokyo Institute of Technology. His research interests are focused on theoretical studies of a broad spectrum of electronic and magnetic phenomena in strongly correlated systems and aim at combining various numerical and analytical tools to understand their microscopic origin and interplay in real materials, including multiferroics, quantum magnets, and topological materials.

behaviour in solids but distinguishing anionic electrons from valence electrons is still not trivial. Moreover, conventional wisdom regarding the stability of materials dictates certain rules that do not apply to electrides, such as electrons residing within atomic orbitals, or charge states of chemical formulae summing to 0. Together these factors have led to electrides being long overlooked and confusion still remains regarding their behaviour, stability and applicability.

We will introduce the distinct types of electride found in the literature, discuss what they have in common with each other and how they differ from everything else. There are previous reviews in the field to which we refer the interested reader,<sup>11,12</sup> but in this work we temper our overview of past results with design principles, guidelines and interpretations not reported in the literature before now. In doing so we are also able to show that electrides are far more prevalent among existing materials than was thought until now. Furthermore, we show that even though electrides have already surpassed expectations in terms of their applicability, they hold yet more promise for exciting and novel applications in the future.

## 2 Organic electrides

The first reports detailing the separation of electrons from parent atoms were reported for alkali metals in solvated systems.<sup>13</sup> In 1907, Charles Kraus proposed that potassium ionizes in liquid ammonia to produce electrons that become components of the solution, similar to dissolved ions. These electrons noticeably affect macroscopic properties such as colour and viscosity,<sup>14</sup> and enable unique and powerful reactions to occur.

Attempts were made to crystallise the alkali solutions in order to freeze the solvated electrons off-atom. The first reported success was *via* evaporation to form thin-films. The solution contained an alkali metal and an organic molecule designed to sterically protect and stabilise the cations with

electron donating groups, thus reducing the overall energy penalty for having a detached electron upon crystallisation.<sup>15</sup> Shortly afterwards the first single crystal was reported using a similar approach and given the name electride. The compound in question was a caesium crown-ether complex, reported by Issa and Dye in 1982.<sup>16,17</sup> Since then, several more electrides have been reported, with similar organic ligands and other alkali metals e.g., K,<sup>18</sup> Cs,<sup>19</sup> Li,<sup>20</sup> and Rb.<sup>21</sup> These materials have come to be referred to as “organic electrides”. Compounds called alkalides are closely related to these organic electrides. Alkalides are solids in which an alkali metal behaves as an anion,<sup>22</sup> which is unusual as these elements are considered among the least electronegative in the periodic table. With the alkali anions in the crystal, the material is a conventional, charge neutral solid in which every electron can be allocated to an atom. However, without the alkalide anion, there is an additional electron in the structurally active role of anion that would define an electride.<sup>23</sup> Thus, there is no unambiguous origin for organic electrides, either solvated alkali metal or alkalide, indicating a surprising richness to the underlying phenomena that leads to their formation.

In fact, there are many computational studies predicting electride properties for other alkali-ligand complexes,<sup>24,25</sup> fullerenes,<sup>26</sup> multi-cage molecules,<sup>27</sup> and alkali-doped polymer chains,<sup>28</sup> predominantly in pursuit of the large non-linear optical responses for these systems. In experiment, however, these complex salts are notoriously unstable with respect to air and moisture exposure,<sup>23</sup> because the exposed anionic electrons are vulnerable to attack from ambient electrophilic species. They are also temperature sensitive, because while they are solid, they are most akin to molecular crystals, which are characterised by a relatively weak internal bonding between the separate clusters. Consequently, it is expected that their use will be limited compared to periodic inorganic solids that are held together by much stronger forces and have more tightly bound/protected electrons.



Wei Ren

*Wei Ren is a professor of physics at Shanghai University, working in the field of computational condensed matter physics, materials science, and quantum electronics. He completed his PhD at The University of Hong Kong in 2006, worked as postdoc at Hong Kong University of Science and Technology, and then research assistant professor at University of Arkansas before 2013. In 2014 he founded the International Centre for Quantum and Molecular Structures at Shanghai University.*



Lee A. Burton

*Lee Burton finished his PhD in the UK in 2014. He was subsequently awarded post-doctoral fellowships (to work in Japan and Belgium) and the European Seal of Excellence 2018. Now he is starting a group at Shanghai University supported by the National Science Foundation of China and the Shanghai Municipal Government. His work originally focussed on materials for photovoltaics, transitioning to crystal structure prediction and, most recently, screening all known materials for applications from catalysis to hydrogen storage. Now he aims to use his expertise with big-data to incorporate machine learning into the process of property prediction and materials discovery.*

However, given the endless possible functionalisation of organic molecules there is no reason to believe these systems will forever remain unusable. For example, it is possible to cross-link the organic exterior of organometallic complexes to form a metal organic framework (MOF) in a popular field of science known as reticular chemistry. Given the remarkable progress with MOFs, especially redox active MOFs, that are stable with respect to charge transfer processes,<sup>29</sup> it seems only a matter of time before a MOF electride can be identified. These would be solids held together by ionic forces, between the ion and the ligand, and covalent forces between the ligands, making a much more stable solid than a molecular crystal.

The stability of organic electrides can in fact be seen to be improving along such a path. While the first organic electrides employed crown ethers that are geometrically planar, requiring 2 to fully encapsulate each cation,<sup>17</sup> a more recent case uses a 3D molecular cage, as shown schematically in Fig. 1. It is a sodium ion in a multidentate cryptand complex denoted as  $\text{Na}^+(\text{TriPip222})\text{e}^-$ .<sup>30</sup> The result is an electride that is more stable than those reported previously, even at or above room temperature, although still not with respect to exposure to moisture or oxygen.<sup>30</sup> While the term 'organic electride' is used throughout the literature to describe this type of system,<sup>31,32</sup> the term can be misleading. As we have shown, organic electrides are in fact organometallic complexes composed of alkali metals and organic molecules and would perhaps more accurately be described as hybrid electrides. Nevertheless, we conform to this convention to help differentiate these electrides from some of the other related yet distinct electrides that are known to exist. Readers seeking more information on this type of electride are referred to the review of Wagner and Dye,<sup>23</sup> however, for the subsequent sections we consider the alternatives, those broadly referred to as 'inorganic electrides'.

### 3 Activated electrides

The previous section introduced the earliest electrides, but this section will detail a more recent example that arguably has spurred the greatest interest in the field.

Mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) is a neutral mineral, first characterised in 1936,<sup>33</sup> that is named after the city Mayen in west Germany.<sup>34</sup> This material is known as a constituent of alumina cement and no electroactive function has been reported in this

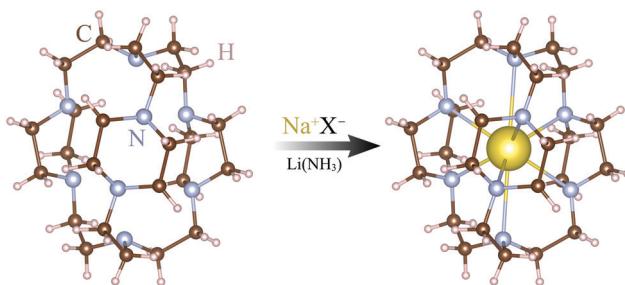


Fig. 1 Example of an 'organic' electride formed from the alkali metal Na, and the organic cryptand TriPip222.<sup>30</sup>

form. However, it can be transformed into an electro-active species: an electride.

Chemically, mayenite exists as an ionic framework of Ca, Al and O atoms in the  $I\bar{4}3d$  symmetry (No. 220). The structure is composed of 12 so-called cages per unit cell, in which there are pore voids. The framework is positively charged but within the pores there are ( $\text{O}^{2-}$ ) counteranions that form the overall charge neutral mineral, shown in Fig. 2. The framework ions are fixed but the oxygen counterions in the voids are relatively loosely bound, able to migrate through openings that connect the pores to each other. With appropriate treatment the charged oxygen counterions can be coaxed out of the material, departing as neutral oxygen molecules and leaving behind 2 excess electrons that make mayenite an electride.<sup>32,35</sup> For this reason we consider mayenite an "activated electride".

The fully-reduced mayenite was first reported in 2003,<sup>37</sup> that is to say a crystal composed of only the positively charged framework and the electrons in the pores, although partially reduced mayenite was reported as far back as 1987.<sup>47</sup> In fact, even in the earliest study of this material, difficulty is reported in characterising and assigning a reasonable ratio of oxygen ions in the crystal,<sup>33</sup> which is prescient of what would become a material famous for anion deficiency.

There are several ways to refer to mayenite. ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) can be equivalently written as  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  but the community has taken to the shorthand notation of 'C12A7', perhaps confusingly given that the C for Ca could be mistaken for carbon, of which there is none in the material. An additional notation is used to distinguish the forms of mayenite, which is a colon followed by the cage content *e.g.* C12A7: $\text{O}^{2-}$  or C12A7: $\text{e}^-$  for the conventional and electride forms of the material respectively.

Mayenite in the electride form does not always need to be reduced from the mineral form, it can be synthesised directly from commercially available constituents.<sup>42</sup> In fact, there are many different ways of making or activating mayenite, which we summarise in Table 1. However, if one does choose to start from the oxidised form of mayenite and reduce it to the electride form, the material transitions from having an

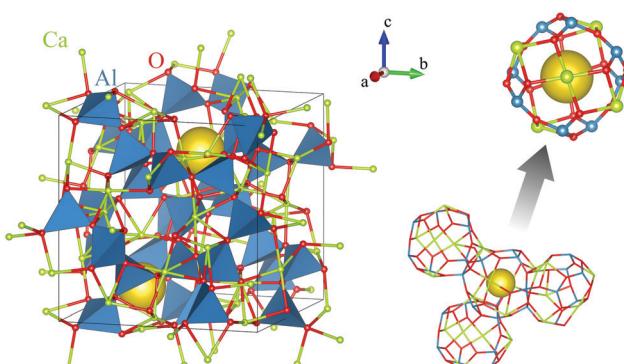


Fig. 2 (left) The unit cell of mayenite with Al–O octahedra in blue and anionic electron density in yellow. (right) The immediate bonding environment of the cage units of mayenite showing their interconnected nature. The crystal structure is taken from Büssem and Eitel.<sup>36</sup>

**Table 1** Summary of C12A7 electride preparation process, adapted from Kim *et al.*<sup>32</sup>

Process type	Process name	Precursor	Reaction process	Ref.
Chemical	Ca vapour reduction	Single crystal	$C_{12}A_7:O^{2-} + 2Ca \rightarrow C_{12}A_7:e^- + 2CaO$	Matsuishi <i>et al.</i> <sup>37</sup>
	Ti vapour reduction	Single crystal/powder	$C_{12}A_7:O^{2-} + Ti \rightarrow C_{12}A_7:e^- + TiO_x$	Hosono <i>et al.</i> <sup>38</sup>
	Melt-solidification	None specified	$C_2^{2-} \rightarrow C_{12}A_7:C_2^{2-} \rightarrow C_{12}A_7:e^- + 2C$	Kim <i>et al.</i> <sup>39</sup>
	CO gas treatment	Single crystal/powder	$C_{12}A_7:O^{2-} + CO \rightarrow C_{12}A_7:e^- + CO_2$	Kim <i>et al.</i> <sup>40</sup>
	Direct synthesis	Powder	$24CaO + 13Al_2O_3 + 2Al \rightarrow C_{12}A_7:e^-$	Jiang <i>et al.</i> , <sup>41</sup> Li <i>et al.</i> <sup>42</sup>
	Sol-gel	Thin-film	$2Ca(C_7H_{15}COO)_2 + Al(OCH(CH_3)_2)_3 \rightarrow C_{12}A_7:e^-$	Chavhan <i>et al.</i> <sup>43</sup>
	Spray pyrolysis	Thin-film	$Ca(C_2H_5COO)_2 + C_6H_{12}AlNO_3 \rightarrow C_{12}A_7:e^-$	Temeche <i>et al.</i> <sup>44</sup>
	Ion implantation	Thin film	$C_{12}A_7:O^{2-} \rightarrow C_{12}A_7:e^- + 1/2O_2$	Miyakawa <sup>45</sup>
Physical	UV reduction	Thin film	$C_{12}A_7:OH^- \rightarrow C_{12}A_7:H^- + 1/2O_2 \xrightarrow{UV} C_{12}A_7:e^- + H_2$	Miyakawa <i>et al.</i> <sup>46</sup>

electronic band gap of  $>3.7$  eV to 0 eV.<sup>48,49</sup> As such the material itself can exhibit a large range of tunable physical properties depending on the concentration of anionic electrons, which has already shown to be a consequential control parameter for macroscopic attributes, such as the glass transition temperature.<sup>50</sup>

The mayenite framework has also proven robust with respect to presence of alternate ions in the pore space. Once the  $O^{2-}$  ions leave the structure they can be replaced with alternate counterions, such as OH,<sup>51</sup> F,<sup>52</sup> Cl,<sup>52</sup> H,<sup>53</sup> Au,<sup>54</sup> Pt,<sup>55</sup> and even the rare-earth elements Gd, Er, Ce, Tb, Eu, Eu.<sup>56</sup> The resulting properties are as versatile as the ions that can be intercalated in the cages are diverse: when OH is encapsulated, mayenite shows a high oxidative potential, able to oxidise benzene, methane and platinum metal;<sup>51</sup> with Pt, mayenite can hydrogenate nitro-arenes better than Pt alone;<sup>55</sup> with hydride intercalated, it shows a rare combination of transparency and conductivity;<sup>53</sup> and the rare-earth doped mayenite show strong visible light emmission after UV irradiation.<sup>53</sup>

The mayenite cage itself can also undergo cation substitution, as has been shown for Sn and Si in experiment,<sup>35</sup> which was able to generate favourable transparent conducting properties for use in electronics and fuel cells. Finally, bulk mayenite can be surface decorated/functionalised for catalysis. Perhaps most famously with Ru nanoparticles to catalyse the Haber–Bosch process of synthesising ammonia,<sup>31,32,57</sup> a process that otherwise has been relatively unchanged for almost a century. The principle underlying the effectiveness of the electride is that the high-energy anionic electron is available to drive the  $N_2$  cleavage, leading to a significantly greater turn over frequency and lower activation energy.<sup>58</sup>

Unlike the organic electrides discussed in the previous section, even when mayenite is fully reduced the material is thermally stable under ambient conditions.<sup>37</sup> The stability is thought to come from the insulating external framework shielding the anionic electron from electrophilic attack. In the case of ammonia synthesis, it has also been demonstrated that mayenite is stable with respect to chemical poisoning, in that as an electride it has the ability to absorb hydrogen as a hydride that prevents smothering of the Ru active site.<sup>9</sup>

$12SrO \cdot 7Al_2O_3$  with the same crystal structure as C12A7 has been made,<sup>59</sup> but it does not show the same degree of stability as mayenite. However, there is no intrinsic reason why the rigid framework would need to be identical to mayenite to exhibit similar properties. The key feature of the framework structure

appears to be caged pores with openings between them that allow ions to be either extracted or loaded, which is certainly not unique to this material.

Early work considered mayenite a zeolite, because of its ability to reversibly absorb water over a wide range of temperatures without changing structure.<sup>47</sup> Certainly, there are different zeolyte materials that could also exhibit the key feature of interconnected pores, given the large number of different possible zeolite structures.<sup>60</sup> In fact, it has been shown possible to start with porous silica zeolite and create an electride by introducing caesium to release electrons to the system, with cation-to-electron ratios reported to be 1 : 1.<sup>61</sup> However, it is widely accepted that the term zeolite refers to aluminosilicates,<sup>62</sup> which would preclude mayenite as it does not contain silicon.

More recently, mayenite has been described as an “anti-zeolite”,<sup>63</sup> to refer to the fact that the framework is positively charged with negative counterions, rather than a negatively charged framework with positively charged counterions, as is the case for zeolites.<sup>64</sup> Interestingly, recent work reports anti-zeolite solids that are positively charged borate frameworks that can also host a range of guest counter-anions.<sup>65</sup> Of several materials reported in this work they report the direct observation of free careers in  $LiBa_{12}(BO_3)_7F_4$ , which could indicate that this material is another rigid-framework electride, just like  $C_{12}A_7:e^-$ .

The intended goal of this section is to introduce mayenite, summarise the properties and convince the reader of its many uses. But most importantly we hope to have shown that mayenite is not unique. The framework can host a variety of counter anions, there are multiple different methods of synthesis and there are alternate crystal frameworks, both zeolite and “anti-zeolite” available. In the opinion of the authors, this suggests that the field of electride chemistry is on the cusp of a rapid expansion that will inevitably lead to a broad range of discoveries and possible utilities in many areas, even if only a few other materials can show the diverse electrochemistry of mayenite.

Finally, there are several reviews in the literature devoted solely to mayenite, to which we refer the interested reader for more detail.<sup>31,32,57</sup>

## 4 High-pressure electrides

The previous section detailed mayenite and other materials that can be transformed from an electronically inert state to

electrides *via* chemical or physical treatment. It is also possible to create electrides using high-pressure to squeeze electrons off the valence shell and into structurally active roles.<sup>66,67</sup>

The oldest-known and most straight-forward examples of high-pressure electrides are the high-pressure alkali metals, that were long noted to have surprising properties. It was expected that a material would approach an ideal metal as pressure increased,<sup>68</sup> whereas alkali metals were observed to begin as almost ideal metals under ambient conditions and become semimetallic or even insulating under pressure. Furthermore, conventional wisdom dictates that a material will compress under pressure, but over a certain pressure range some alkali metals would expand—generally proceeding from body-centred cubic to face-centred cubic to non-close packed atomic arrangements.<sup>69</sup> Eventually, it was noted that the pressure induces an electron transition from the valence shell to interstitial regions of the structure, where the electron begins to play the role of anion,<sup>70</sup> *i.e.* form an electride.

The amount of pressure needed to trigger this transition depends on the valence state of the atom.<sup>71</sup> With increasing pressure, the energies of the valence orbitals of atoms increase more rapidly than do the possible interstitial states. Given enough pressure the frontier atomic electron may become higher in energy than interstitial states, resulting in electron transfer to the interstitial space between ions,<sup>72</sup> forming an electride. For the lighter alkali metals under pressure the transition is associated with an s-to-p orbital transition,<sup>73</sup> whereas the heavier Cs undergoes an s-to-d orbital transition.<sup>74</sup> The exact energy is not trivial to predict because the formation of the electride form is usually accompanied by a phase transition, *i.e.* atomic reconfiguration in response to the off-atom electron density.

Electride phases have been shown to occur for many elements under high pressure, for example Na,<sup>67</sup> K,<sup>75</sup> Li,<sup>76</sup> Mg,<sup>77</sup> and Cs, which was already described as an electride in 1987.<sup>74</sup> At high enough pressures, even elements that are not considered electropositive show electride transitions, for example, aluminium is predicted to develop ‘blobs’ of off-atom electron density at terapascal pressures.<sup>78</sup> After a metal has become an electride, further increasing pressure can transform the system back to a metal again, which is referred to in the literature as a ‘reentrant’ metal.<sup>68</sup>

It is fair to say that computational studies have led the way on studying high-pressure compounds because of the relatively ease of performing high-pressure calculations compared to high-pressure experiments.<sup>80</sup> Nevertheless, experiment has been able to confirm calculated structures and properties, even among some of the most unintuitive states. Sodium has been shown to transform into a dense, insulating material that is optically transparent at around 200 GPa<sup>67</sup> and lithium was shown to transform from a metal to a semiconductor at 80 GPa.<sup>76</sup>

Remarkably, even helium, the most inert of elements, has shown the ability to form an electride at high pressure, although in compound form. At pressures greater than 113 GPa, Na<sub>2</sub>He forms a clear electride with an electron pair located within a crystal

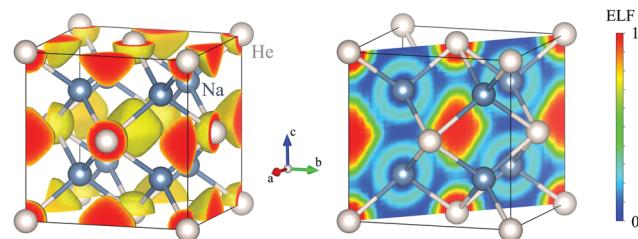


Fig. 3 Electron localisation function (ELF) of high-pressure Na<sub>2</sub>He (in agreement with Dong *et al.*<sup>79</sup>).

cavity as shown in Fig. 3. The helium atoms do not participate in any bonding themselves but the electron pairs can be considered as a multi-centre atomic bond.<sup>79</sup> There are other, varied and interesting compounds that are predicted to be electrides at high pressure. For example, the systems of Al–S,<sup>81</sup> Li–N,<sup>82</sup> Mg–O,<sup>83</sup> Na–Cl,<sup>84</sup> and Li–O,<sup>85</sup> have predicted stable compounds that behave as electrides under sufficient pressure, to name just a few.

More fundamental approaches to electron behaviour predict such behaviour to be almost ubiquitous under the right amount of pressure,<sup>70,86</sup> which is reflected in the variety of compounds and elements we see in the literature and suggests that materials scientists will be able to find an electride form for almost any given system under the right external conditions.

That said, the word electride is not always used to define such behaviour. There are several other terms used to refer to high-pressure electrides and their interstitial electron density. High pressure potassium is referred to as a pseudo-binary ionic compound,<sup>75</sup> for high pressure Li and Mg the interstitial electron density is referred to as ‘interstitial quasiatoms’,<sup>77</sup> and the term electride may not be used at all. A high-pressure phase of Li, for example, has been reported to show a “large interstitial electron density accumulation” but the word electride is not used in the paper.<sup>68</sup> We will consider these ideas in greater detail in the discussion section of this paper, where we attempt to draw conclusions on the nature of electrides based on all of the different types of electride, including the high-pressure phases.

The existence, prevalence and properties of high-pressure electrides are of interest in the field of astrochemistry, planetary geology, xenobiology *etc.* For example, one of the unique features of the earth that makes it a suitable place for life to develop is the geomagnetic field that is generated by metals at high pressure in the interior of the planet. Since there are high-pressure electrides with predicted magnetic properties,<sup>87</sup> for systems that are not magnetic in the ambient ground-state, it raises implications for our understanding of the universe, and our place within it. We will continue on to discuss magnetic electrides later in the article, but first, it is instructive to consider so-called native electrides.

## 5 Native electrides

We have previously discussed treatment-activated or pressure-induced electrides. Now we turn to a class of electrides that have been referred to as ‘native’,<sup>88</sup> or ‘natural’ electrides,<sup>4</sup>

which is to say they exist as electrides without treatment or extrinsic condition.

Perhaps the most famous native electride is  $\text{Ca}_2\text{N}$ , where the calcium ions donate a total of 4 electrons but the nitrogen can only accept 3. The additional electrons aggregate in delocalised layers that alternate with the bonded  $[\text{Ca}-\text{N}]^+$  forming an overall charge neutral crystal.<sup>89</sup> It has been predicted that even monolayers of the bonded sheets retain electride properties,<sup>90</sup> with persistence of 2-dimensional electron gas for individual layers.

$\text{Ca}_2\text{N}$  is what is often referred to as a 2-dimensional (2D) electride. This nomenclature has been incorporated and extended to apply to other electrides, based on the degree of freedom of the anionic electron density that characterises them as such. Thus the 2D electrides are materials with anionic electrons delocalised in a plane, 1D electrides are materials where anionic electrons are delocalised in a channel and 0D electrides are materials in which anionic electrons are localised to a single point in the structure. Examples of each of these electride types can be seen in Fig. 4. Interestingly mayenite most closely conforms to a 0D electride, because the anionic electrons exist in the cavity of the framework, ostensibly coordinated between 6 calcium atoms. However the electron still can move between cages *via* a hopping mechanism.<sup>91</sup>

There are literally hundreds of native electrides predicted from a variety of computational studies.<sup>88,92–94</sup> To understand what this means fully it should be known that in general there are two different approaches to computational discovery, even within the same level of theory. The first is structure prediction, which is achieved using an algorithm to generate structures whose energy is then checked with density functional theory.<sup>95,98</sup> The structure with the lowest energy for any given chemical formula can be taken to be indicative of a new compound, that may or may not be an electride. New compounds can also be predicted by substituting chemical species in templates provided by the known electrides.<sup>96,97</sup> The second computational approach is predicting electride properties by taking crystal

structures reported from experimental and calculating the ground-state electron density for this structure. This approach usually relies on repositories of structure data files such as the inorganic crystal structure database (ICSD),<sup>99</sup> or the materials project.<sup>100</sup>

Both of these approaches have their advantages and disadvantages. Structure prediction algorithms, available *via* packages such as USPEX,<sup>101</sup> can perform exhaustive potential energy landscape samplings, but the level of theory may not be rigorous enough to provide accurate energy landscapes to sample. Data mining experimental structures, on the other hand, may include errors or incomplete information. For example, a significant number of entries in the ICSD were reported using X-ray diffraction (XRD) techniques at a time when it wasn't possible for routine XRD to reliably identify hydrogen atoms.<sup>102</sup> Calculations may then be predicting electride forms of what were in fact hydride materials.

Regardless, the true identification of a native electride ultimately relies on experimental proof, which is not trivial and certainly not routine.<sup>103</sup> To the knowledge of the authors, the following are the only materials to have been concluded to be natural electrides from experimental evidence:  $\text{Ca}_2\text{N}$  and  $\text{Y}_2\text{C}$  by direct observation of the excess electron density by angle resolved photoemission spectroscopy (ARPES);<sup>104,105</sup>  $\text{Y}_5\text{Si}_3$  by Hard X-ray Photoelectron Spectroscopy (HAXPES) and Ultra-violet photoelectron spectroscopy (UPS);<sup>106</sup>  $\text{CeH}_2$  and  $\text{LaH}_2$  by thermal desorption spectroscopy,<sup>107</sup> and  $\text{Sr}_2\text{N}$  and  $\text{Sr}_3\text{CrN}_3$  by neutron diffraction.<sup>108,109</sup>

$\text{Ca}_2\text{N}$ ,  $\text{Sr}_2\text{N}$  and  $\text{Y}_2\text{C}$  are isostructural 2-dimensional electrides, with a trigonal structure in  $R\bar{3}m$  symmetry.  $\text{Y}_5\text{Si}_3$  and  $\text{Sr}_3\text{CrN}_3$  are both 1-dimensional electrides in hexagonal structures with  $P6_3/mcm$  and  $P6_3/m$  symmetries respectively.  $\text{LaH}_2$  and  $\text{CeH}_2$  are 0-dimensional electrides in cubic systems with  $Fm\bar{3}m$  symmetry.

Mostly these electrides are relatively unstable, with reportedly extreme air and moisture sensitivity in experiment.<sup>110</sup> For  $\text{Ca}_2\text{N}$ , an explosive reaction is observed to occur with water, to wit  $\text{Ca}_2\text{N} + 2\text{H}_2\text{O} \rightarrow 2\text{CaO} + \text{NH}_3 + 1/2\text{H}_2$ .<sup>89</sup> This has a predicted reaction enthalpy of around 700 kJ mol<sup>-1</sup> for both  $\text{Ca}_2\text{N}$  and  $\text{Sr}_2\text{N}$ .<sup>111</sup> When  $\text{Ca}_2\text{N}$  is exposed to oxygen the colour change from black to white, consistent with spontaneous oxidation. However, the  $\text{Y}_5\text{Si}_3$  electride is reported to be air and water stable, while still maintaining favourable catalytic performance for ammonia synthesis.<sup>106</sup> Based on this, admittedly small, sample it appears that reactivity directly correlates with the exposure of the anionic electron in 3-dimension space, that is to say 2D electrides are the least stable (*i.e.*  $\text{Ca}_2\text{N}$ ), 1D are somewhat stable (*i.e.*  $\text{Y}_5\text{Si}_3$ ) and 0D can be thermally stable (*i.e.* mayenite).

$\text{Sr}_3\text{CrN}_3$  is also observed to be unstable with respect to oxygen and moisture but is still surprisingly stable considering it contains the redox-active species chromium.<sup>109</sup> Cr is known to exhibit a variable oxidation state, with the 3<sup>+</sup> and 4<sup>+</sup> charge states being relatively close in energy. Thus, it is surprising that Cr in the electride is explicitly found to be 4<sup>+</sup> by X-ray absorption near-edge spectroscopy (XANES), when the ion could take the anionic electron from the structure and become 3<sup>+</sup> instead. In fact, it is often reported that Cr is most stable in the

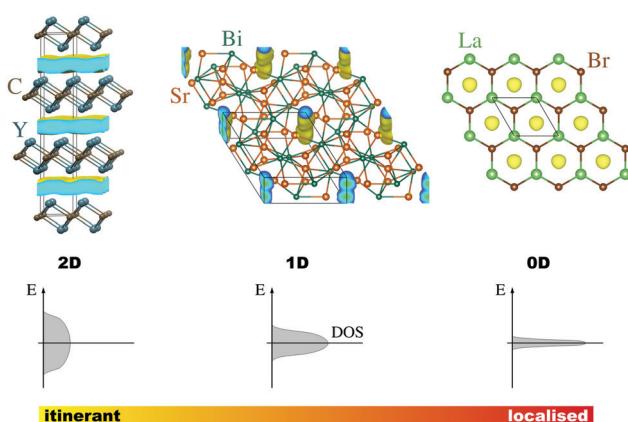


Fig. 4 (top) Examples of 2D ( $\text{Y}_2\text{C}$ , left), 1D ( $\text{Sr}_5\text{Bi}_3$ , centre) and 0D ( $\text{LaBr}_2$ , right) electrides. The anionic electron density resides in a planar, columnar or cavity environments. (bottom) The relationship between electron degree of freedom and density of states (DOS) at the Fermi energy.

$3^+$  state, again making the thermal stability of this electride surprising.<sup>112</sup>

While native electrides are often considered distinct from mayenite because they are not composed of framework and counterion it can be shown that they, like mayenite, do have ‘oxidised’ forms that would not be considered electrides. Given that we saw that  $\text{C}12\text{A}7:\text{e}^-$  can be synthesised directly too, in Section 3, it could be said that native electrides are just as much ‘activated’ by chemical treatment as mayenite.  $\text{LaH}_2$  and  $\text{CeH}_2$  are both reduced forms of isostructural  $\text{LaH}_3$  and  $\text{CeH}_3$  respectively.<sup>107</sup>  $\text{Y}_5\text{Si}_3$  also has a hydride counterpart with an identical structure:  $\text{Y}_5\text{Si}_3\text{H}$ .<sup>113</sup> As we’ve pointed out before it was difficult to resolve hydrogen in earlier work, so it is unclear if there was hydrogen present in the original synthesis reported in 1960.<sup>114</sup>  $\text{Y}_2\text{C}$  also has an isostructural  $\text{Y}_2\text{CH}_2$  phase,<sup>115</sup> as does  $\text{Sr}_2\text{N}$  with  $\text{Sr}_2\text{NH}$ .<sup>116</sup> While the electride  $\text{Sr}_3\text{CrN}_3$  doesn’t have a reported hydride analogue, the isostructural material  $\text{Ba}_3\text{CrN}_3$  does have a known fully stoichiometric hydride form.<sup>117</sup> For all of the hydride forms mentioned here, the  $\text{H}^-$  are expected to reside in the same space in crystal structure that the anionic electron density resides in the electride form. Finally, unlike the other native electrides,  $\text{Ca}_2\text{N}$  saturated with hydrogen forms a different structural phase for  $\text{Ca}_2\text{NH}$ .<sup>118</sup> Rather than a hydride counterpart however, we believe the  $\text{Ca}_2\text{N}$  oxidised form is  $\text{Ca}_2\text{NCl}$  or  $\text{Ca}_2\text{NBr}$ , with the structures for both shown in Fig. 5.<sup>119</sup> The electride form has been achieved by reduction from the non-electride compound  $\text{Ca}_3\text{N}_2$  previously,<sup>89</sup> but this phase is not isostructural to the electride unlike  $\text{Ca}_2\text{NCl}$  or  $\text{Ca}_2\text{NBr}$ .

Thus we have shown that each of the confirmed natural electrides have a possible parent oxidised form, just as does mayenite. From this we do not rule out the possibility that all compound electrides have an oxidation state balanced “native” form, be that hydride, halide or oxide, and it is in the removal of these species that activates the material as an electride. Interesting questions raised by this are what other elements could be removed from a host crystal in stoichiometric amounts that leave behind a stable framework and dissociated electron density? And does the ability to reversible uptake these ions make electrides suitable for ion conduction applications?

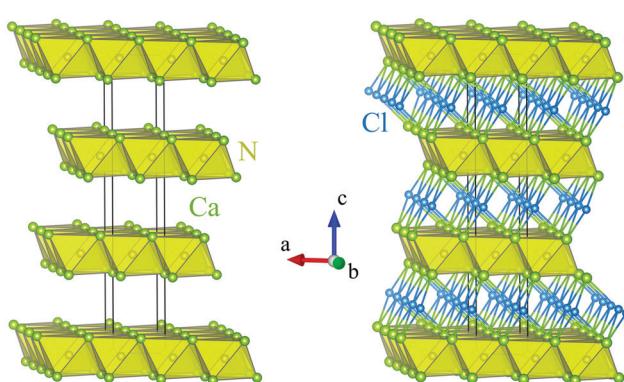


Fig. 5 Crystal structures of  $\text{Ca}_2\text{N}$  (left) and  $\text{Ca}_2\text{NCl}$  (right) from RECKEWEG2002575.

## 6 Magnetic electrides

We showed previously that mayenite as an electride has an overall oxidation state of +2, caused by the removal of an  $\text{O}^{2-}$  ion. This leaves 2 electrons that can form a spin-up and spin-down diamagnetic pair configuration, giving an overall non-magnetic material.<sup>37</sup> However, in other electrides, the anionic electrons can remain unpaired, rendering the bulk material magnetic.

Magnetic properties in an electride could be useful for a variety of applications. For example, nonmagnetic electrides can be used as electron emitters because of the relatively low work function. But an electride in which the anionic electrons possess the same spin properties (which is the origin of bulk magnetism) could be used for spin injection in a spintronic device.<sup>120</sup> The combination of magnetism and low work function would also be ideal for use in magnetic tunnel junctions and other advanced electronic applications.<sup>121</sup> Thus, being able to include magnetism as a materials parameter for the already unique and applicable electrides could open up new opportunities for the materials science community.

Generally speaking, the origins of magnetism in electrides are not expected to be different from conventional magnetic materials. The condition of Stoner instability is known to be useful in predicting and explaining the aspects of magnetic properties. This condition states that if the density of states (DOS) around the Fermi energy ( $E_F$ ) is large, the electrostatic repulsion between electrons can prevent double occupancy. As a result, the highest occupied electronic states can develop spin splitting to lower their energy and the material will be magnetic.

The convention of classifying electrides in terms of their anionic electron degree of freedom (*i.e.* 0D, 1D, 2D) becomes useful here. One can assume that because the anionic electrons are far removed from a parent atom they are relatively high in energy, to the extent they are probably the highest energy populated states in a material *i.e.* the  $E_F$ . Knowing the degree of quantum confinement of states at  $E_F$  allows one to infer the degree of dispersion and therefore the density of states (DOS). If the material is a 2D electride, the anionic electrons are highly delocalised, forming dispersive bands in the electronic structure. Because the bands are dispersive, the density of states at  $E_F$  is relatively small, indicating a weak Stoner instability. As a result, 2D systems with highly itinerant anionic electrons are expected to be metals with an unsteady tendency towards magnetism. In accordance with this idea, the 2D electride  $\text{Y}_2\text{C}$ , which was thought to possibly exhibit magnetism,<sup>122</sup> has shown no static magnetic order even at low temperatures.<sup>123</sup> By contrast, the anionic electrons in a 0D electride are strongly confined spatially. As a result, the bands are weakly dispersive and relatively flat in the electronic structure, leading to a narrow and relatively high DOS at the Fermi level that can lead to a strong Stoner instability. Again in accordance with this idea, the 0D electride  $\beta\text{-Yb}_5\text{Sb}_3$ , in which the anionic electrons are strongly confined within  $\text{Yb}_4$  tetrahedra,<sup>124</sup> has shown to exhibit magnetism in experiment. This relationship is shown schematically in Fig. 4.

To the best of our knowledge,  $\beta\text{-Yb}_5\text{Sb}_3$  is one of only two electrides to have demonstrated magnetic properties in experiment. While it is a confirmed electride, we do not include the material  $\beta\text{-Yb}_5\text{Sb}_3$  in the previous section on native electrides because it is not the ground-state structure of the  $\text{Yb}_5\text{Sb}_3$  system and so the term native is difficult to apply intuitively. Having said that the ground state  $\alpha\text{-Yb}_5\text{Sb}_3$  material is also expected to be an electride,<sup>93</sup> but this has yet to be confirmed by experiment.

$\text{Gd}_2\text{C}$  has recently been found to be an electride that is ferromagnetic above room temperature, *i.e.* has a Curie temperature around 350 K.<sup>125</sup> Unlike our previous discussion seeking out electrides in which the spin of the anionic electron generates magnetism, for this material it is the Gd atoms that are magnetic.  $\text{Gd}_2\text{C}$  is isostructural to  $\text{Ca}_2\text{N}$  with the anionic electrons sandwiched between the bonded plane found to mediate ferromagnetic coupling between the Gd atom layers, to the extent that without them the system is anti-ferromagnetic. Interestingly, the anionic electrons are repeatedly described as strongly localised and occupying specific lattice sites rather than being itinerant within the layer, an assertion that is at odds with the strongly dispersive bands in the electronic structure reported within the same study and the behaviour observed for the other electrides with this structure. Regardless, the material represents an interesting test-case for introducing strong magnetism to electride systems and is certainly worthy of further study. What's more, it is found that Cl atoms can be intercalated between the layers as is the case for  $\text{Ca}_2\text{N}$ , see Fig. 5, and so  $\text{Gd}_2\text{C}$  can probably be considered a new native electride.

While potentially useful for the targeted discovery of new magnetic electrides, the convention of categorising electrides based on their geometric confinement is not complete on a quantum level. For example, the anionic electrons in the predicted 0D electrides  $\text{LaBr}_2$  and  $\text{La}_2\text{Br}_5$  have been calculated to be spatially extended, and their overlap at neighbouring cavities gives rise to ferromagnetism *via* direct exchange.<sup>126,127</sup>

$\text{LaBr}_2$  and  $\text{La}_2\text{Br}_5$  are also theoretically shown to be Mott-insulators.<sup>127</sup> A Mott-insulator transition takes place if the energetic penalty for double occupancy of electrons (the on-site coloumb interaction) is large enough to drive open an energy gap at the Fermi level. When this occurs, a material that would be metallic under an elementary band picture can become a semiconductor or insulator. Such behaviour has also been observed in experiment for the  $\beta\text{-Yb}_5\text{Sb}_3$  electride, which could expand the possible range of applications for electride even further, with potential uses in gas sensors and solar energy.<sup>128</sup>

Many more electrides are predicted to be magnetic *via* computational methods such as DFT than have been found in experiment. For example, the 1D  $\text{A}_5\text{B}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}; \text{B} = \text{As}, \text{Sb}, \text{Bi}$ ), and the 0D  $\text{Sr}_{11}\text{Mg}_2\text{Si}_{10}$ ,  $\text{Ba}_7\text{Al}_{10}$ ,  $\text{Ba}_4\text{Al}_5$  are predicted to be stable magnetic electrides with magnetic energies of up to hundreds of meV.<sup>129</sup> However, a high-throughput study of electrides with spin-polarised calculations indicates that magnetic electrides are still just a small proportion of the materials that can be considered electrides overall.<sup>88</sup>

In summary, 2D and 0D electrides can be regarded as two extreme cases of itineracy of the anionic electrons, with 1D

electride representing an intermediate. Because there is a greater density of states available in 0D and 1D electrides, they are more likely to exhibit magnetic properties.<sup>129</sup> While, the tendency towards Stoner instability will also depend on the hybridization between anionic and orbital electrons, the existing nomenclature pertaining to electrides can help guide the discovery of novel magnetic systems, of which there are unfortunately few known now.

## 7 Topological electrides

In the previous section we showed that electrides can exhibit diverse electronic properties. In fact, owing to the loosely bound nature and geometrical confinement of the anionic electrons, electrides can also be a testbed for realising topological states. This is an area of intense research activity in condensed matter physics,<sup>130</sup> especially in the search for novel topological materials.<sup>131</sup>

Topology is a branch of mathematics pertaining to geometric properties of objects and their possible deformations. For example, a sphere cannot undergo continuous transformation into a torus, and *vice versa*, because there is a hole or 'genus' in the torus but not in the sphere. In the context of condensed matter physics, the electronic states of the Brillouin zone are the object and the Berry phase is the curvature of the object. In reciprocal space, a vacuum and most conventional insulating crystals are topologically trivial, that is to say do not contain a genus. However certain materials are not topological trivial and it is not possible for the band structure to interpolate continuously between these materials and the external vacuum without closing the gap.<sup>132</sup> This forces a symmetry-protected metallic state at the surface of these materials, even if they are insulators inside the bulk.

Topological materials include topological insulators (TIs) with an energy gap in the bulk interior but conducting states at the surface and topological semimetals (TSMs) that are gapless in the bulk and feature symmetry protected surface states, such as Fermi arcs. We can consider band inversions, in which the usual ordering of the conduction and valence bands is inverted, as a typical characteristic of TIs,<sup>133</sup> and symmetry-enforced band crossings as a typical characteristic of TSMs.<sup>134</sup> Various categories of topological semimetals have been proposed, such as nodal line semimetals, Dirac semimetals, Weyl semimetals, nodal surface semimetals, multifold fermion semimetals *etc.*,<sup>134</sup> the details of which are beyond the scope of this article.

$\text{Ca}_3\text{Pb}$  is claimed to be the first topological electride reported in the literature from theoretical calculations.<sup>135</sup> The assignment is based on 'several linear band-crossing points near the Fermi level', two of which are triply degenerate without the inclusion of spin-orbit-coupling (SOC) or Dirac Points with SOC. However, this assignment is refuted elsewhere in the literature,<sup>136</sup> and, in our opinion, an insufficient case is made to support the argument either way. Unfortunately, such confusion and contradiction in the literature is not only found for this case.

The 2D  $\text{Y}_2\text{C}$  has also been proposed to possess a topologically non-trivial electronic state,<sup>136</sup> although the exact nature of these states varies considerably with calculation parameters. In the absence of SOC,  $\text{Y}_2\text{C}$  is predicted to be a nodal-line semimetal, with degenerate valence and conduction bands close to  $E_F$ . Including SOC however, removes the band crossing and gives rise to a gap between the valence and conduction bands. This precludes the assignment of a nodal-line semimetal,<sup>137</sup> but does allow for the identification of topological surface states floating at the surface of  $\text{Y}_2\text{C}$  by a  $Z_2$  topological invariant.<sup>138</sup> The possibility to realise topological states in  $\text{Y}_2\text{C}$  is attributed to the anionic electrons, but due care needs to be taken in considering this assignment. In the previous section we mentioned that  $\text{Y}_2\text{C}$  was predicted to be magnetic in theory but found not to be in experiment. The ferromagnetic spin ordering found in theory shows multiple pairs of the Weyl nodes and drumhead like surface state near  $E_F$ , which are direct evidence of a Weyl semimetal. However, since the material displays no magnetic ordering in experiment down to 2 K,<sup>139</sup> it is unclear to what extent these predictions can be expected to hold. Thus, this one electride has potential to be reported as 3 distinct types of topological material, depending on the level of theory, while possibly being none in experiment.

The predicted electride  $\text{Sc}_2\text{C}$  is isostructural to  $\text{Y}_2\text{C}$  and is expected to exhibit a small band gap with a narrow semi-conducting behaviour.<sup>136</sup> Similar to  $\text{Y}_2\text{C}$ , for a sufficiently thick slab there is predicted to be a surface state in the gap, which is well separated from the bulk states. This surface state originates from a  $\pi$  Zak phase,<sup>140</sup> which is non-zero in the entire Brillouin zone, allowing  $\text{Sc}_2\text{C}$  to be considered a Zak phase insulator. Interestingly, the topological state does not come from atomic orbitals, as shown in Fig. 6, instead it is floating at the surface, mostly composed of anionic electrons. Such a prediction can be considered typical of why electrides might be ideal candidates for exploration of topological materials, because of their unique anionic electron density.

Zhang *et al.*<sup>141</sup> proposed the family of  $\text{A}_2\text{B}$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}; \text{B} = \text{Sb}, \text{Bi}$ ) compounds as topological nodal line electrides.

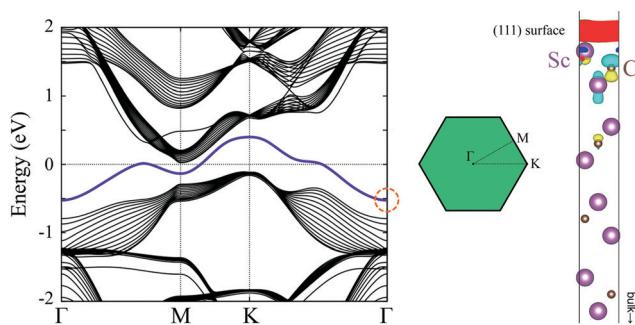


Fig. 6 (left) Electronic band structure for the (111) surface of a slab of  $\text{Sc}_2\text{C}$  in the GGA+ $U$ , taken from Hirayama *et al.*<sup>136</sup> The purple band represents the topological surface state originating from the quantized  $\pi$  Zak phase, and the corresponding wave function of the topological surface state at the  $\Gamma$  point (indicated by the dotted circle) is shown on the right.

These materials possess structures that have  $I4/mmm$  with inversion and time-reversal symmetries and phonon dispersion calculations show they are all dynamically stable. Calculated band structures showed these electrides exhibited two nodal lines along the high symmetry points of the Brillouin zone without SOC, but with SOC a small gap was induced in the crossing points for each material. Still, they posited that if the nodal lines could be entirely contributed by the anionic electrons, which are unconstrained by the nuclei, SOC would have a weak impact on the nodal lines even with heavy elements in the material. And so, electrides are good candidates to further pursue these class of topological systems, even with elements that may not be suitable in more conventional materials.

The symmetry protected surface state of topological materials are responsible for various quantum Hall effects.<sup>142–144</sup> Incidentally, several predicted topological materials were later shown to also be electrides. For example, a quantum anomalous Hall insulator  $\text{LaBr}$ ,<sup>145–147</sup> quantum spin Hall system  $\text{HfBr}$ , and a nodal-line semimetal  $\text{Sr}_2\text{Bi}$ .<sup>136</sup> Thus, the nature of topological states and electride electronic configuration are closely related.

To summarize, the anionic electrons in electrides can provide unique states to allow for the realisation of topological states. There are established design principles for searching out or creating topological materials available,<sup>148</sup> and electrides are a good class of material in which to implement them. Because the topological states of these compounds are closely related to anionic electrons near the Fermi level, they not only occupy the lattice in three-dimensional space, they can also contribute high-speed carriers at two-dimensional boundaries. The interested reader is referred to the paper of Hirayama *et al.*,<sup>136</sup> devoted to this topic.

Unfortunately, however, it is clear that great care needs to be taken in the theoretical prediction of electronic properties for electrides, especially when it comes to topological applications. Most theoretical studies of electrides have been limited to standard schemes within DFT, such as local density approximation (LDA)<sup>149</sup> and generalised gradient approximation (GGA)<sup>150,151</sup> for the exchange–correlation functional.

Quite generally, the anionic electrons in 2D electrides can be regarded as a two-dimensional electron gas, where non-local electronic correlations and dynamical screening that are not included at the level of LDA or GGA may become important. In this case, one can resort to the so-called GW approximation that includes many-body effects in a perturbative manner.<sup>152,153</sup> For example, the electronic structure calculations within GW reveal a narrow gap in  $\text{Y}_2\text{C}$ , excluding a nodal-line semimetal scenario predicted within GGA (without spin–orbit coupling), as we discussed, and the GW calculations should be considered more reliable.

Several modifications of DFT exist to include the effects of strong electron correlations. These can take the form of semi-empirical or mean-field methods, such as hybrid functionals,<sup>154,155</sup> and DFT+ $U$ ,<sup>156</sup> and they have proved useful in describing many properties of d- and f-electron systems. However their use may not be suitable for 0D electrides with localised magnetic moments because the on-site Coulomb

repulsion ( $U$  parameter) can only be applied to atomic orbitals, which for anionic electrons is not of direct relevance. For electrides it may be necessary to resort to effective models constructed solely for the anionic states and solve them directly by using many-body techniques. For example, the Hubbard-type model was constructed for  $\text{LaBr}_2$  and  $\text{La}_2\text{Br}_5$  by using the Wannier functions representing the anionic electrons.<sup>127</sup>

Overall, the exploration of topological properties in electrides appears barely to have begun to scratch the surface of the rich materials chemistry and physics we see here. Especially in this section, we see a real demand for experimental characterisation to help guide and support the theoretical community in identifying the crucial features of topological materials that are so sensitive to theoretical parameters. This, in turn, provides an opportunity for high-impact work to be performed at the cutting edge of materials science.

## 8 Intermetallic electrides

To date several experiments have reported intermetallic electrides. Among all the different types of electrides we've discussed in this paper these are the most difficult to classify and generalise.

The definition of an intermetallic compound is "a solid phase involving two or more metallic or semimetallic elements with an ordered structure and often a well-defined and fixed stoichiometry".<sup>157</sup> To the knowledge of the authors, the materials reported as intermetallic electrides are  $\text{CaAlSi}$ ,  $\text{SrAlSi}$ ,  $\text{BaAlSi}$ ,<sup>158</sup>  $\text{La}_3\text{Cu}_2\text{Si}_4$ ,<sup>159</sup>  $\text{Y}_3\text{Pd}_2$ ,<sup>160</sup> and  $\text{LaRuSi}$ .<sup>161</sup> It can be seen that these compounds do conform to the definition of an intermetallic compound, but then again, so do the native electrides  $\text{Sr}_3\text{CrN}_3$ ,  $\text{Y}_5\text{Si}_3$  and Mayenite.

The justification given for this classification of electride in literature is the observation of "an interstitial band crossing the Fermi level, which coincides with the presence of the electron density peak at the vacant site X" and similar properties compared to the known electrides  $\text{C}12\text{A}7:\text{e}$  and  $\text{Ca}_2\text{N}$ ".<sup>159</sup> The intermetallic compounds also conform to the majority of the defining features of electrides observed for the other systems, such as the presence of strongly donating cations. They have also been shown to perform as superior catalysts when compared to other materials,<sup>159</sup> perhaps as a result of low work function, which we have seen is typical for electrides. Although it seems the term 'intermetallic' is often employed when the oxidation states of component species are not trivial to assign.

Incidentally, a high-throughput DFT study that employed a similar physical description of electrides predicted  $\text{LaRuSi}$  as an electride, along with other such cases as  $\text{PrScGe}$ ,  $\text{NdScGe}$ , which may yet also prove to be electrides. However, in the same study, it is possible to see systems that could be considered as simple intermetallic compounds, returned alongside the known electrides. Systems such as  $\text{NdGa}$ ,  $\text{BaSn}$ ,  $\text{Nd}_3\text{In}$  and  $\text{Sr}_3\text{Li}_2$  among others.<sup>88</sup>

The question "Are Intermetallic Phases Electrides?" was already posed decades ago,<sup>163</sup> and was assessed by comparing

crystal structures between electrides and intermetallics. But, while they find close agreement, this is not likely to be helpful as intermetallic compounds are not defined by their structures and intermetallics in general do not have detailed bond counting rules developed for them.<sup>163,164</sup> So how are electrides to be effectively distinguished from regular intermetallics, or indeed, regular metals?

As an example, aluminum is considered to approach an "ideal" metal or free electron gas. The valence electrons move relatively freely, unaffected by the presence of the metal ions. The electron density of metal bonding in aluminium is shown in Fig. 7, which agrees with experimentally observed electron density reported previously.<sup>162</sup> This is very similar to the off-atom electron density found in electrides (see for example the high-pressure  $\text{Na}_2\text{He}$  electride ELF shown in Fig. 3). Since the justification behind assignment of intermetallic electrides relies on the same off-site electron density as can be seen in a ground state metal,<sup>159,160</sup> we encounter a problem with accepting this as the defining physical characteristic of an electride. Because there are many known intermetallic compounds with alkali and alkali earth elements that are not electrides but do show the same electronic behaviour,<sup>165</sup> care should be taken in assigning labels that could arbitrarily split the field.

Furthermore,  $\beta\text{-Yb}_5\text{Sb}_3$ , discussed in Section 6, is referred to as intermetallic in the literature and conforms to the official definition.<sup>166</sup> Both  $\beta\text{-Yb}_5\text{Sb}_3$  and  $\text{Y}_3\text{Pd}_2$  exhibit anionic electron density within a cluster of cations (Yb or Y, respectively) in the structure.<sup>160</sup> This behaviour is similar to zintl compounds, where electron density is shared within a clusters of ions, but for the zintl phases the clusters are of anions not cations. Zintl compounds are also closely related to intermetallics,<sup>167</sup> often contain alkali elements and,<sup>168</sup> since the extra electrons are shared between multiple sites, they can also be considered to have off-atom electron density. In fact, a study screening the original experimental reports of materials predicted to be electrides found that a significant fraction were described as zintl compounds at the time they were characterised.<sup>88</sup>

Zintl compounds are subject to exhaustive studies elsewhere.<sup>169</sup> In this section, we merely wish to show that zintl compounds are closely related to electrides, which are both in turn, closely related to intermetallic compounds. These terms can offer a handle on a deeper history of relevant chemistry that

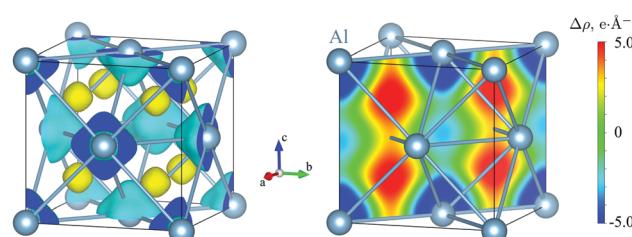
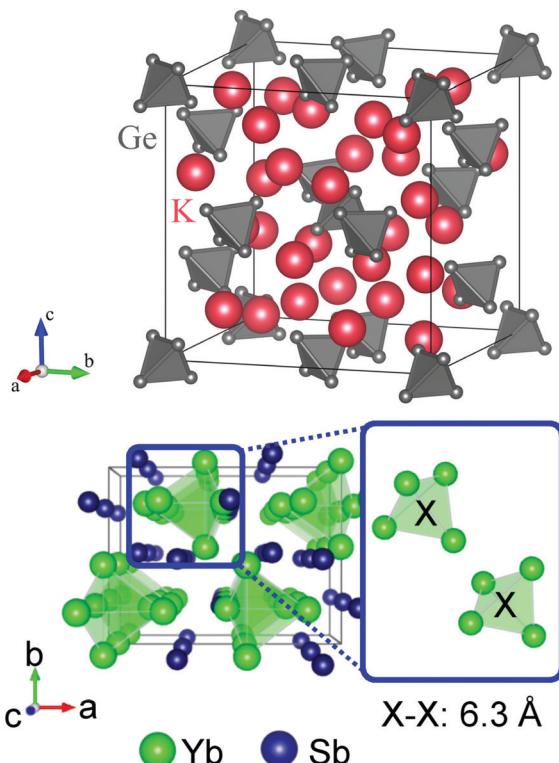


Fig. 7 The deformation electron density map  $\Delta\rho$  of aluminium, as calculated with DFT (in agreement with Nakashima *et al.*<sup>162</sup>). It shows clear lobes of off atom electron density in the ground state metal, which could be taken as indicating electride behaviour if only this defining characteristic is evoked.



**Fig. 8** (top) KGe, an archetypal example of a zintl compounds, with internal Ge<sub>4</sub> clusters and (bottom) the structure of β-Yb<sub>5</sub>Sb<sub>3</sub>, in which the anionic electrons are confined within Yb<sub>4</sub> tetrahedra from Lu *et al.*<sup>124</sup>

may be of interest to those who seek to harness the properties of electrides but they also highlight possible areas of confusion and misidentification. To further illustrate this idea, the crystal structure of an archetypal zintl compound, KGe,<sup>170</sup> is shown in Fig. 8 alongside the crystal structure of β-Yb<sub>5</sub>Sb<sub>3</sub> from Lu *et al.*<sup>124</sup> showing how they might be confused.

The intermetallic electrides discussed in this section may well be electrides, but while in every previous section of this paper we have concluded that the community is poised to discover ever more, in the case of intermetallic electrides we advise more caution in the use of the term. In the subsequent section we will devote attention explicitly to the definitions involved in what one might and might not consider an electride.

## 9 Discussion

The sections of this paper are labelled along lines that we found useful during manuscript preparation. Some of the labels are taken from the literature, *e.g.* ‘organic’ and ‘intermetallic’ electride, and some we created ourselves, *e.g.* in the literature mayenite is not referred to as an ‘activated’ electride. The sections of this paper are not intended to be definitive, nor are they intended to indicate mutually exclusive aspects of electrides. That is to say that there can be overlap in the properties, for example, there are predicted to be high-pressure, magnetic, organic electrides.<sup>171</sup> Over the coarse of this article,

especially in the previous section, we showed that unequivocally distinguishing electrides can be difficult. That difficulty may arise from the lack of adherence to traditional concepts, which also makes electrides difficult to define.

The original and most common definition of an electride is a system in which one or more electrons behave as anions.<sup>172,173</sup> But how does this hold now that we as a community consider Ca<sub>2</sub>N an electride, where the anion has shown to be delocalised to the extent that it behaves as an effective 2-dimensional electron gas?<sup>90</sup> At the same time, it is the deviation away from free electron behaviour in alkali metals that mark them as electrides at high pressure. These seemingly contradictory behaviours pose a difficult in answering the question: what are electrides? To the knowledge of the authors, this is the first article to consider such a broad swathe of electrides simultaneously, specifically with these difficulties in mind, and so this section will be devoted to comparing and contrasting the various properties of the electrides that we have introduced. Ultimately, we propose an alternative definition of what it means to be an electride that we have not seen reported before.

A feature that often arises in our discussion of electrides is sum of oxidation states to greater than zero. However, the very concept of oxidation state is arbitrary because the charge on a given ion is not an observable. The assigned charge relies on a choice of model to partition the electron density between atoms and there is no unambiguous way to do so.<sup>174</sup> If one requires that oxidation states sum to more than zero in electrides then they can be confused with zintl and intermetallic compounds. Moreover the recent identification of the first electride to contain a redox active element, *i.e.* Cr in Sr<sub>3</sub>CrN<sub>3</sub>,<sup>109</sup> highlights the flexibility inherent in oxidation states. Thus we find that chemical formula or the correspondingly assigned charges are an unsuitable method of identifying electrides, even though this consideration has been used as a design principle previously.<sup>96</sup>

Another feature that appears common to all electrides is the presence of strongly electron-donating or electropositive cations. This is intuitive as the anionic electron must be pushed in to the structure by one of the atomic species. If one considers the measured work function of phase pure elements as related to the electropositive nature of cations, it can be seen that electrides do contain the elements with the smallest values. In fact, the only elements not found among electrides with smaller work functions are Ce, Eu, Rb, Sm and Tb.<sup>175</sup> While considerations such as this can be instructive for the targeted discovery of new native electrides, it is not applicable to high-pressure electrides, where even a He compound, or Al metal, are shown to form electrides at high enough pressure. There are also many conventional materials containing electropositive cations that could not be considered electrides, for example CaO is not an electride but Ca<sub>12</sub>Al<sub>14</sub>O<sub>32</sub> is. As such, the presence of electropositive cation cannot be the basis of a universal definition of electrides either.

Even the small number of candidates we consider known electrides up to now show a wide variety of crystal structure

motifs, the only attribute they have in common at first glance is a vacant space where the electron can reside. However, simple consideration of void space is insufficient to distinguish electrides as the anionic electron almost always resides in one of the smaller pores of the structure because the electron distribution allows the surrounding cations to draw closer together. Indeed, the cation–electron distance is even smaller than the cation–anion distance in some cases.<sup>88</sup> Considering the myriad porous frameworks in chemistry, such as zeolites, molecular sieves and MOFs *etc.* that should not be confused with electrides, crystal structure also does not appear to be a defining feature. We mentioned in the previous section that observation of the electron density also cannot uniquely identify electrides. Sn(II) compounds, for example, have lone pairs that are structurally active,<sup>176</sup> and occupy sites that otherwise could host an anion,<sup>177</sup> but are not electrides. It has been suggested that electrides can be distinguished from lone pair systems because the off-atom electron density is isotropic, rather than directional.<sup>178</sup> However, this consideration brings us back to the electron density profiles of ground state metals. In Fig. 7, we showed the valence electron density map for aluminium, which has clear lobes of off-atom electron density. These could be taken as indicative of electride behaviour if only this characteristics of electrides is evoked. We believe that the answer can not lie in electron density profiles alone, because off-atom electron density associated with multi-centre bonding is ubiquitous in metals and intermetallic compounds.

Bonding considerations are often used to define chemical systems. However, it has been shown for a compound electride that the origin of the anionic electron state is provided by orbital overlap of cation states to form a multi-centre bond,<sup>95</sup> which, again, is the same for ground-state metals. Furthermore, we find contradictory bonding behaviour between electrides. For the case of the high-pressure alkaline metals the system begins as a pure metal that can be described as a nearly free electron system and as it becomes an electride it becomes less metallic and more ionic.<sup>75</sup> Conversely, in the case of mayenite the conventional system is purely ionic and as it becomes an electride it becomes less ionic and more metallic. Somewhere between the limits of ionic and metallic lie the bonding characteristics of an electride but so too does the behavior of almost any compound. A recent study on the nature of bonding reports 5 categories of bonding mechanism,<sup>179</sup> which are supported by experiment<sup>180</sup> (not including the weaker hydrogen- and halogen-bonding in materials).<sup>181</sup> The quantifiable bonding behaviour underlying metallic and ionic bonding represents extremes of the bonding spectrum, as shown in Fig. 9. We also saw that, like oxidation states, bonding paradigms can not always be applied for systems such as intermetallic compounds,<sup>163,164</sup> which are closely related to electrides. Thus, we also do not believe that electrides can be defined by their internal bonding behaviour.

Finally then, can electrides be considered distinct from conventional materials at all? We have shown that many compound electrides can be reduced from conventional materials and that the difference in properties between these forms is

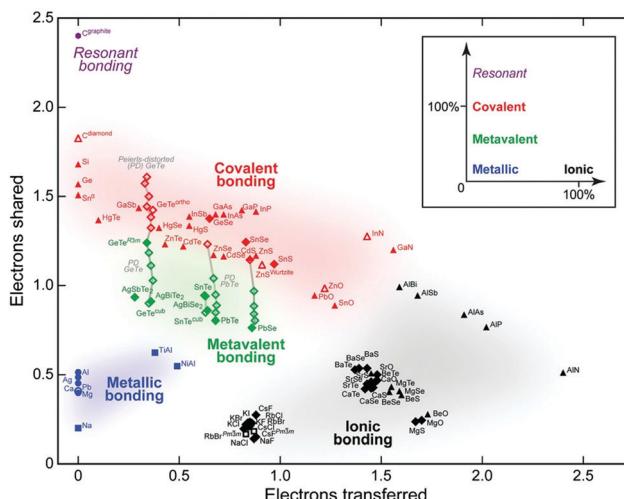


Fig. 9 An example attempt to categorise materials based on bonding paradigms, showing that metallic and ionic bonding cover a huge range of materials chemistry.<sup>179</sup>

potentially very large. But there must be a regime between fully oxidised and fully reduced where anionic electrons contribute to the phase of the material but are not ubiquitous throughout. Under such conditions the anionic electrons can be considered analogous to a Farbe center or ‘F-centre’ defect. These are a type of crystallographic impurity in which an anionic vacancy in a crystal lattice is occupied by electron(s).<sup>182</sup> These have been discussed for mayenite previously, but not for native electrides, because their oxidised forms are not considered often in the literature, and not for organic electrides because, again, they are not often related back to the alkalides analogues. In the context of this work a single F-centre can be considered as an electride-like scenario at the most dilute limit and, as the concentration of defects increases, the material becomes more electride-like. Thus it could be said that electrides are distinct from conventional compounds but related by the underlying phenomena of anion vacancy formation. In this light, electrides represent an extreme on a spectrum of defect concentration, which is already known to manifest a large range of materials properties. Unfortunately this idea can NOT be applied when considering high-pressure electrides because in this case pure elements can form electride phases with no anion deficiency or vacancy formation.

Taking all of this information into account, we offer an alternate, though perhaps still flawed, approach to defining electrides.

The band structures of oxidised and reduced mayenite are shown in Fig. 10. In  $\text{C}12\text{A}7:\text{O}^{2-}$  there are states provided by the  $\text{O}^{2-}$  that are localised. It can be seen in the relative flatness of the valence band leading to poor conductivity in the bulk material. As it is reduced, the  $\text{O}^{2-}$  ions and the corresponding states are removed and the electrons are forced to occupy higher energy states that are more delocalised, seen in the dispersiveness of the bands, leading to higher conductivities. The shifting up in the energy of the valence occupied states is seen in the shift in Fermi energy and is the origin of the low

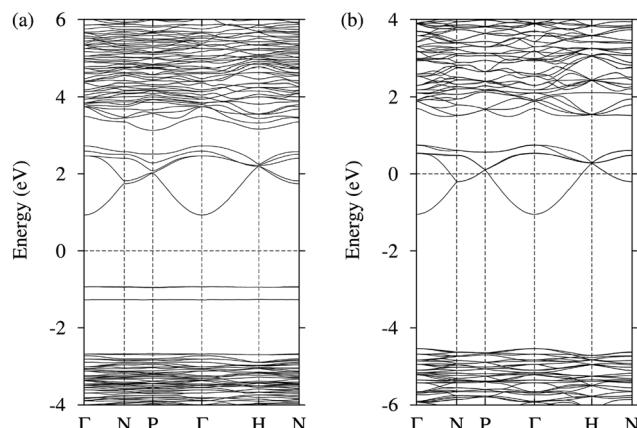


Fig. 10 The band structure of oxidised (a) and reduced mayenite (b) from Lobo *et al.*<sup>183</sup>

work function reported for this material. A similar observation can be made for the native electrides in that  $\text{Ca}_2\text{N}$  can be considered reduced from the parent compound  $\text{Ca}_2\text{NCl}$ ,<sup>119</sup> and the organic electrides can be considered reduced forms of their alkalide precursors.<sup>22</sup>

Given that we've shown that electrides are not conventional, and almost always require some treatment to induce their state, it could be said that: electrides are material in which non-ground state electronic configurations of a conventional material are permanently populated *via* chemical or physical stress.

The use of 'non-ground electronic configuration' in our definition contrasts with excited states in a semiconductor under photon irradiation, for example, which decay to the ground state almost instantaneously even under continued light exposure. Over time an equilibrium that provides a new quasi-Fermi level for that semiconductor can be attained but it is still a dynamic system. Hence our use of the word permanent, even though of course the high pressure could be reduced or a chemical oxidation could reverse a reduction in order to return an electride to its conventional state.

Our definition is still flawed because it requires that for every electride there is an identified conventional counterpart. For the intermetallic electrides such a definition fails because there is no parent compound, and the lack of adherence to simple chemical rules of intermetallic compounds means that there are unlikely to be any. However, our definition does prevent ground state metals such as aluminium from being convoluted with electrides and, by relating electrides to a parent conventional material allows for the consideration of vacancies or F-centre defects, without excluding high-pressure electrides that contain no defects. In fact, for all of the other systems discussed in this paper, we believe it works well and even goes some way to explain the latent properties one would expect of an electride, *e.g.* a relatively small work function.

Ultimately, however, it will almost always fall to the intuition of trained chemists, physicists and engineers to decide what may or may not be an electride. Hopefully taking into account the observations made in this article.

## 10 Conclusions

In this paper we have introduced the many distinct types of electride present in the literature. In doing so we've traced the arc of development of these systems from chemical curiosity to industrially robust catalyst and testbed for cutting edge condensed matter physics.

To the knowledge of the authors, no other article has brought together such disparate areas of electride chemistry to be examined simultaneously, perhaps for good reason. By considering electron density, internal bonding, crystal structure, defects and properties, we attempt to elucidate what electrides have in common, to what extent they can be unique and offer an alternative definition of what it means to be an electride. These should all help to stimulate research in the field, which has repeatedly shown to be a worthwhile endeavor.

While electrides are new and exciting, we have shown that the underlying physical phenomenon that defines electrides has a long and robust history. Even until recently, multiple works that are either closely related to electrides or explicitly about them do not use the word electride, whether it is high-pressure alkali metals,<sup>68</sup> or intermetallic zintl compounds.<sup>167</sup> Thus we can assume that the underlying properties of electrides are prevalent far beyond what we had the opportunity to discuss in this review. Furthermore, theoretical studies are returning possible new electride candidates faster than can be reasonably confirmed in experiment. For these and other reasons, we believe that the community is on the cusp of finding that materials are more flexible in their stability with respect to bound electrons than was thought possible previously.

Finally, in highlighting the difficulties in distinguishing electrides from regular materials we arrive at our overall conclusion which is that electrides *are* regular materials. To deny that is to deny the quantum nature of electrons themselves. And while the use of the word is instructive and categorisation of materials can be conceptually beneficial, as a community we must ensure that artificial models created for the sake of convenience, such as oxidation state and charge neutrality, do not hold us back from making use of the rich materials science available.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors would like to thank Profs Aron Walsh and Jeffrey Reimers for useful discussion. Fig. 1–5, 7 and 8 were made with VESTA software.<sup>184</sup> This work was supported by the National Natural Science Foundation of China (Grant No. 51950410585, 51672171, 51861145315 and 51911530124), Shanghai Municipal Science and Technology Commission Program (No. 19010500500), and Independent Research Project of State Key Laboratory of Advanced Special Steel and Shanghai Key Laboratory of Advanced Ferrometallurgy at Shanghai University.

## References

- 1 R. H. Huang and J. L. Dye, *Chem. Phys. Lett.*, 1990, **166**, 133–136.
- 2 H. Hosono, S.-W. Kim, S. Matsuishi, S. Tanaka, A. Miyake, T. Kagayama and K. Shimizu, *Philos. Trans. R. Soc., A*, 2015, **373**, 20140450.
- 3 J. Hu, B. Xu, S. A. Yang, S. Guan, C. Ouyang and Y. Yao, *ACS Appl. Mater. Interfaces*, 2015, **7**, 24016–24022.
- 4 S. Guan, S. Y. Huang, Y. Yao and S. A. Yang, *Phys. Rev. B*, 2017, **95**, 165436.
- 5 H.-M. He, Y. Li, H. Yang, D. Yu, S.-Y. Li, D. Wu, J.-H. Hou, R.-L. Zhong, Z.-J. Zhou, F.-L. Gu, J. M. Luis and Z.-R. Li, *J. Phys. Chem. C*, 2017, **121**, 958–968.
- 6 S. Watanabe, T. Watanabe, K. Ito, N. Miyakawa, S. Ito, H. Hosono and S. Mikoshiba, *Sci. Technol. Adv. Mater.*, 2011, **12**, 034410.
- 7 N. Kuganathan, A. Chroneos and R. W. Grimes, *Sci. Rep.*, 2019, **9**, 13612.
- 8 T.-N. Ye, J. Li, M. Kitano and H. Hosono, *Green Chem.*, 2017, **19**, 749–756.
- 9 M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S.-W. Kim, M. Hara and H. Hosono, *Nat. Chem.*, 2012, **4**, 934–940.
- 10 Y. Toda, H. Hirayama, N. Kuganathan, A. Torrisi, P. V. Sushko and H. Hosono, *Nat. Commun.*, 2013, **4**, 1–8.
- 11 S. Zhao, E. Kan and Z. Li, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2016, **6**, 430–440.
- 12 S. G. Dale and E. R. Johnson, *J. Phys. Chem. A*, 2018, **122**, 9371–9391.
- 13 J. L. Dye and M. G. DeBacker, *Annu. Rev. Phys. Chem.*, 1987, **38**, 271–299.
- 14 C. A. Kraus, *J. Am. Chem. Soc.*, 1907, **29**, 1557–1571.
- 15 J. L. Dye, M. R. Yemen, M. G. DaGue and J. Lehn, *J. Chem. Phys.*, 1978, **68**, 1665–1670.
- 16 D. Issa and J. L. Dye, *J. Am. Chem. Soc.*, 1982, **104**, 3781–3782.
- 17 A. Ellaboudy, J. L. Dye and P. B. Smith, *J. Am. Chem. Soc.*, 1983, **105**, 6490–6491.
- 18 D. L. Ward, R. H. Huang and J. L. Dye, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, **44**, 1374–1376.
- 19 M. J. Wagner, R. H. Huang, J. L. Eglin and J. L. Dye, *Nature*, 1994, **368**, 726–729.
- 20 R. H. Huang, M. J. Wagner, D. J. Gilbert, K. A. Reidy-Cedergren, D. L. Ward, M. K. Faber and J. L. Dye, *J. Am. Chem. Soc.*, 1997, **119**, 3765–3772.
- 21 Q. Xie, R. H. Huang, A. S. Ichimura, R. C. Phillips, W. P. Pratt and J. L. Dye, *J. Am. Chem. Soc.*, 2000, **122**, 6971–6978.
- 22 B. Van Eck, L. D. Le, D. Issa and J. L. Dye, *Inorg. Chem.*, 1982, **21**, 1966–1970.
- 23 M. J. Wagner and J. L. Dye, *Annu. Rev. Mater. Sci.*, 1993, **23**, 223–253.
- 24 W. Chen, Z.-R. Li, D. Wu, Y. Li, C.-C. Sun, F. L. Gu and Y. Aoki, *J. Am. Chem. Soc.*, 2006, **128**, 1072–1073.
- 25 S. G. Dale and E. R. Johnson, *Phys. Chem. Chem. Phys.*, 2017, **19**, 12816–12825.
- 26 Y.-F. Wang, Z.-R. Li, D. Wu, C.-C. Sun and F.-L. Gu, *J. Comput. Chem.*, 2010, **31**, 195–203.
- 27 Z.-B. Liu, Y.-C. Li, J.-J. Wang, Y. Bai, D. Wu and Z.-R. Li, *J. Phys. Chem. A*, 2013, **117**, 6678–6686.
- 28 H.-L. Xu, Z.-R. Li, D. Wu, B.-Q. Wang, Y. Li, F. L. Gu and Y. Aoki, *J. Am. Chem. Soc.*, 2007, **129**, 2967–2970.
- 29 J. Calbo, M. J. Golomb and A. Walsh, *J. Mater. Chem. A*, 2019, **7**, 16571–16597.
- 30 M. Y. Redko, J. E. Jackson, R. H. Huang and J. L. Dye, *J. Am. Chem. Soc.*, 2005, **127**, 12416–12422.
- 31 K. Khan, A. K. Tareen, M. Aslam, K. H. Thebo, U. Khan, R. Wang, S. S. Shams, Z. Han and Z. Ouyang, *Prog. Solid State Chem.*, 2019, **54**, 1–19.
- 32 S.-W. Kim, S. Matsuishi, M. Miyakawa, K. Hayashi, M. Hirano and H. Hosono, *J. Mater. Sci.: Mater. Electron.*, 2007, **18**, 5–14.
- 33 W. Buessem and A. Eitel, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1936, **95**, 175–188.
- 34 K. W. B. John, W. Anthony, R. A. Bideaux and M. C. Nichols, *Handbook of Mineralogy*, Mineralogical Society of America, Chantilly, VA, USA, 2003.
- 35 K. Khan, A. K. Tareen, U. Khan, A. Nairan, S. Elshahat, N. Muhammad, M. Saeed, A. Yadav, L. Bibbò and Z. Ouyang, *Sci. Rep.*, 2019, **9**, 1–9.
- 36 W. Büssem and A. Eitel, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1936, **95**, 175–188, DOI: 10.1524/zkri.1936.95.1.175.
- 37 S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka and H. Hosono, *Science*, 2003, **301**, 626–629.
- 38 H. Hosono, S.-W. Kim, S. Matsuishi, S. Tanaka, A. Miyake, T. Kagayama and K. Shimizu, *Philos. Trans. R. Soc., A*, 2015, **373**, 20140450.
- 39 S. Kim, M. Miyakawa, K. Hayashi, T. Sakai, M. Hirano and H. Hosono, *J. Am. Chem. Soc.*, 2005, **127**, 1370–1371.
- 40 S.-W. Kim, K. Hayashi, M. Hirano, H. Hosono and I. Tanaka, *J. Am. Ceram. Soc.*, 2006, **89**, 3294–3298.
- 41 D. Jiang, Z. Zhao, S. Mu, H. Qian and J. Tong, *Inorg. Chem.*, 2019, **58**, 960–967.
- 42 F. Li, X. Zhang and H. Liu, *J. Am. Ceram. Soc.*, 2020, **103**, 35–42.
- 43 P. Chavhan, A. Sharma, R. Sharma, G. Singh and N. Kaushik, *Thin Solid Films*, 2010, **519**, 18–23.
- 44 E. Temeche, E. Yi, V. Keshishian, J. Kieffer and R. M. Laine, *J. Eur. Ceram. Soc.*, 2019, **39**, 1263–1270.
- 45 M. Miyakawa, *J. Ceram. Soc. Jpn.*, 2009, **117**, 395–401.
- 46 M. Miyakawa, K. Hayashi, M. Hirano, Y. Toda, T. Kamiya and H. Hosono, *Adv. Mater.*, 2003, **15**, 1100–1103.
- 47 H. Hosono and Y. Abe, *Inorg. Chem.*, 1987, **26**, 1192–1195.
- 48 J. A. McLeod, A. Buling, E. Z. Kurmaev, P. V. Sushko, M. Neumann, L. D. Finkelstein, S.-W. Kim, H. Hosono and A. Moewes, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 045204.
- 49 M. M. Rashad, A. G. Mostafa, B. W. Mwakikunga and D. A. Rayan, *Appl. Phys. A: Mater. Sci. Process.*, 2016, **123**, 42.
- 50 L. E. Johnson, P. V. Sushko, Y. Tomota and H. Hosono, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 10007–10012.

- 51 J. Imlach, L. D. Glasser and F. Glasser, *Cem. Concr. Res.*, 1971, **1**, 57–61.
- 52 J. Jeevaratnam, F. P. Glasser and L. S. D. Glasser, *J. Am. Ceram. Soc.*, 1964, **47**, 105–106.
- 53 K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano and H. Hosono, *Nature*, 2002, **419**, 462–465.
- 54 M. Miyakawa, H. Kamioka, M. Hirano, T. Kamiya, P. V. Sushko, A. L. Shluger, N. Matsunami and H. Hosono, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 205108.
- 55 T.-N. Ye, Z. Xiao, J. Li, Y. Gong, H. Abe, Y. Niwa, M. Sasase, M. Kitano and H. Hosono, *Nat. Commun.*, 2020, **11**, 1020.
- 56 Y. Liu, L. Ma, D. Yan, H. Zhu, X. Liu, H. Bian, H. Zhang and X. Wang, *J. Lumin.*, 2014, **152**, 28–32.
- 57 S. Kim and H. Hosono, *Philos. Mag.*, 2012, **92**, 1–33.
- 58 M. Hara, M. Kitano and H. Hosono, *ACS Catal.*, 2017, **7**, 2313–2324.
- 59 H. Hosono, S. W. Kim, M. Miyakawa, S. Matsuishi and T. Kamiya, *J. Non-Cryst. Solids*, 2008, **354**, 2772–2776.
- 60 C. Baerlocher, L. McCusker and D. Olson, *Atlas of Zeolite Framework Types*, Elsevier Science, 2007.
- 61 A. S. Ichimura, J. L. Dye, M. A. Cambor and L. A. Villaescusa, *J. Am. Chem. Soc.*, 2002, **124**, 1170–1171.
- 62 P. Jacobs, E. Flanigen, J. Jansen and H. van Bekkum, *Introduction to Zeolite Science and Practice*, Elsevier Science, 2001.
- 63 S. G. Ebbinghaus, H. Krause and F. Syrowatka, *Cryst. Growth Des.*, 2013, **13**, 2990–2994.
- 64 C. J. Rhodes, *Sci. Prog.*, 2010, **93**, 223–284.
- 65 T. B. Bekker, V. P. Solntsev, S. V. Rashchenko, A. P. Yelisseyev, A. V. Davydov, A. A. Kragzhda, A. E. Kokh, A. B. Kuznetsov and S. Park, *Inorg. Chem.*, 2018, **57**, 2744–2751.
- 66 B. Wan, J. Zhang, L. Wu and H. Gou, *Chin. Phys. B*, 2019, **28**, 106201.
- 67 Y. Ma, M. Eremets, A. R. Oganov, Y. Xie, I. Trojan, S. Medvedev, A. O. Lyakhov, M. Valle and V. Prakapenka, *Nature*, 2009, **458**, 182–185.
- 68 T. Matsuoka, M. Sakata, Y. Nakamoto, K. Takahama, K. Ichimaru, K. Mukai, K. Ohta, N. Hirao, Y. Ohishi and K. Shimizu, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **89**, 144103.
- 69 H. Katzke and P. Tolédano, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 184101.
- 70 B. Rousseau and N. W. Ashcroft, *Phys. Rev. Lett.*, 2008, **101**, 046407.
- 71 M.-S. Miao and R. Hoffmann, *Acc. Chem. Res.*, 2014, **47**, 1311–1317.
- 72 B. Rousseau, Y. Xie, Y. Ma and A. Bergara, *Eur. Phys. J. B*, 2011, **81**, 1–14.
- 73 N. Christensen and D. Novikov, *Solid State Commun.*, 2001, **119**, 477–490.
- 74 H. G. von Schnering and R. Nesper, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1059–1080.
- 75 M. Marqués, G. J. Ackland, L. F. Lundgaard, G. Stinton, R. J. Nelmes, M. I. McMahon and J. Contreras-García, *Phys. Rev. Lett.*, 2009, **103**, 115501.
- 76 T. Matsuoka and K. Shimizu, *Nature*, 2009, **458**, 186–189.
- 77 M.-S. Miao and R. Hoffmann, *J. Am. Chem. Soc.*, 2015, **137**, 3631–3637.
- 78 C. J. Pickard and R. J. Needs, *Nat. Mater.*, 2010, **9**, 624–627.
- 79 X. Dong, A. R. Oganov, A. F. Goncharov, E. Stavrou, S. Lobanov, G. Saleh, G.-R. Qian, Q. Zhu, C. Gatti, V. L. Deringer, R. Dronskowski, X.-F. Zhou, V. B. Prakapenka, Z. Konôpková, I. A. Popov, A. I. Boldyrev and H.-T. Wang, *Nat. Chem.*, 2017, **9**, 440–445.
- 80 H. L. Skriver, *Phys. Rev. Lett.*, 1982, **49**, 1768–1772.
- 81 S. Shao, W. Zhu, J. Lv, Y. Wang, Y. Chen and Y. Ma, *npj Comput. Mater.*, 2020, **6**, 11.
- 82 Y.-M. Chen, H.-Y. Geng, X.-Z. Yan, Z.-W. Wang, X.-R. Chen and Q. Wu, *Chin. Phys. B*, 2017, **26**, 056102.
- 83 Q. Zhu, A. R. Oganov and A. O. Lyakhov, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7696–7700.
- 84 W. Zhang, A. R. Oganov, A. F. Goncharov, Q. Zhu, S. E. Boulfelfel, A. O. Lyakhov, E. Stavrou, M. Somayazulu, V. B. Prakapenka and Z. Konôpková, *Science*, 2013, **342**, 1502–1505.
- 85 X. Dong, J. Hou, J. Kong, H. Cui, Y.-L. Li, A. R. Oganov, K. Li, H. Zheng, X.-F. Zhou and H.-T. Wang, *Phys. Rev. B*, 2019, **100**, 144104.
- 86 F. Siringo, R. Pucci and G. G. N. Angilella, *High Press. Res.*, 1997, **15**, 255–264.
- 87 S. Dong and H. Zhao, *Appl. Phys. Lett.*, 2012, **100**, 142404.
- 88 L. A. Burton, F. Ricci, W. Chen, G.-M. Rignanese and G. Hautier, *Chem. Mater.*, 2018, **30**, 7521–7526.
- 89 D. Gregory, A. Bowman, C. Baker and D. Weston, *J. Mater. Chem.*, 2000, **10**, 1635–1641.
- 90 D. L. Druffel, K. L. Kuntz, A. H. Woomer, F. M. Alcorn, J. Hu, C. L. Donley and S. C. Warren, *J. Am. Chem. Soc.*, 2016, **138**, 16089–16094.
- 91 P. V. Sushko, A. L. Shluger, K. Hayashi, M. Hirano and H. Hosono, *Thin Solid Films*, 2003, **445**, 161–167.
- 92 J. Zhou, L. Shen, M. Yang, H. Cheng, W. Kong and Y. P. Feng, *Chem. Mater.*, 2019, **31**, 1860–1868.
- 93 Q. Zhu, T. Frolov and K. Choudhary, *Matter*, 2019, **1**, 1293–1303.
- 94 Y. Tsuji, P. L. V. K. Dasari, S. F. Elatresh, R. Hoffmann and N. W. Ashcroft, *J. Am. Chem. Soc.*, 2016, **138**, 14108–14120.
- 95 J. Wang, K. Hanzawa, H. Hiramatsu, J. Kim, N. Umezawa, K. Iwanaka, T. Tada and H. Hosono, *J. Am. Chem. Soc.*, 2017, **139**, 15668–15680.
- 96 T. Tada, S. Takemoto, S. Matsuishi and H. Hosono, *Inorg. Chem.*, 2014, **53**, 10347–10358.
- 97 T. Inoshita, S. Jeong, N. Hamada and H. Hosono, *Phys. Rev. X*, 2014, **4**, 031023.
- 98 Y. Zhang, H. Wang, Y. Wang, L. Zhang and Y. Ma, *Phys. Rev. X*, 2017, **7**, 011017.
- 99 M. Hellenbrandt, *Crystallogr. Rev.*, 2004, **10**, 17–22.
- 100 A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Mater.*, 2013, **1**, 011002.
- 101 C. W. Glass, A. R. Oganov and N. Hansen, *Comput. Phys. Commun.*, 2006, **175**, 713–720.

- 102 C. C. Wilson, *Crystallogr. Rev.*, 2007, **13**, 143–198.
- 103 C. Fortmann, C. Niemann and S. H. Glenzer, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 174116.
- 104 J. S. Oh, C.-J. Kang, Y. J. Kim, S. Sinn, M. Han, Y. J. Chang, B.-G. Park, S. W. Kim, B. I. Min, H.-D. Kim and T. W. Noh, *J. Am. Chem. Soc.*, 2016, **138**, 2496–2499.
- 105 K. Horiba, R. Yukawa, T. Mitsuhashi, M. Kitamura, T. Inoshita, N. Hamada, S. Otani, N. Ohashi, S. Maki, J.-I. Yamaura, H. Hosono, Y. Murakami and H. Kumigashira, *Phys. Rev. B*, 2017, **96**, 045101.
- 106 Y. Lu, J. Li, T. Tada, Y. Toda, S. Ueda, T. Yokoyama, M. Kitano and H. Hosono, *J. Am. Chem. Soc.*, 2016, **138**, 3970–3973.
- 107 H. Mizoguchi, M. Okunaka, M. Kitano, S. Matsuishi, T. Yokoyama and H. Hosono, *Inorg. Chem.*, 2016, **55**, 8833–8838.
- 108 N. E. Brese and M. O'Keeffe, *J. Solid State Chem.*, 1990, **87**, 134–140.
- 109 P. Chanhom, K. E. Fritz, L. A. Burton, J. Kloppenburg, Y. Filinchuk, A. Senyshyn, M. Wang, Z. Feng, N. Insin, J. Suntivich and G. Hautier, *J. Am. Chem. Soc.*, 2019, **141**, 10595–10598.
- 110 A. S. Bailey, R. W. Hughes, P. Hubberstey, C. Ritter, R. I. Smith and D. H. Gregory, *Inorg. Chem.*, 2011, **50**, 9545–9553.
- 111 A. Walsh and D. O. Scanlon, *J. Mater. Chem. C*, 2013, **1**, 3525–3528.
- 112 H.-J. Lunk, *ChemTexts*, 2015, **1**, 6.
- 113 I. McColm, V. Kotroczo, T. Button, N. Clark and B. Bruer, *J. Less-Common Met.*, 1986, **115**, 113–125.
- 114 E. Parthé, *Acta Crystallogr.*, 1960, **13**, 868–871.
- 115 J. Maehlen, V. Yartys' and B. Hauback, *J. Alloys Compd.*, 2003, **351**, 151–157.
- 116 T. Sichla, F. Altorfer, D. Hohlwein, K. Reimann, M. Steube, J. Wrzesinski and H. Jacobs, *Z. Anorg. Allg. Chem.*, 1997, **623**, 414–422.
- 117 N. W. Falb, J. N. Neu, T. Besara, J. B. Whalen, D. J. Singh and T. Siegrist, *Inorg. Chem.*, 2019, **58**, 3302–3307.
- 118 M. Kitano, Y. Inoue, H. Ishikawa, K. Yamagata, T. Nakao, T. Tada, S. Matsuishi, T. Yokoyama, M. Hara and H. Hosono, *Chem. Sci.*, 2016, **7**, 4036–4043.
- 119 O. Reckeweg and F. J. DiSalvo, *Solid State Sci.*, 2002, **4**, 575–584.
- 120 S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova and D. M. Treger, *Science*, 2001, **294**, 1488–1495.
- 121 B.-C. Min, K. Motohashi, C. Lodder and R. Jansen, *Nat. Mater.*, 2006, **5**, 817–822.
- 122 T. Inoshita, N. Hamada and H. Hosono, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, **92**, 201109.
- 123 M. Hiraishi, K. M. Kojima, I. Yamauchi, H. Okabe, S. Takeshita, A. Koda, R. Kadono, X. Zhang, S. Matsuishi, H. Hosono, K. Hirata, S. Otani and N. Ohashi, *Phys. Rev. B*, 2018, **98**, 041104.
- 124 Y. Lu, J. Wang, J. Li, J. Wu, S. Kanno, T. Tada and H. Hosono, *Phys. Rev. B*, 2018, **98**, 125128.
- 125 S. Y. Lee, J.-Y. Hwang, J. Park, C. N. Nandadasa, Y. Kim, J. Bang, K. Lee, K. H. Lee, Y. Zhang, Y. Ma, H. Hosono, Y. H. Lee, S.-G. Kim and S. W. Kim, *Nat. Commun.*, 2020, **11**, 1526.
- 126 J. Zhou, Y. P. Feng and L. Shen, 2019, arXiv:1904.04952.
- 127 D. I. Badrtdinov and S. A. Nikolaev, *J. Mater. Chem. C*, 2020, DOI: 10.1039/D0TC01223H.
- 128 S. B. Roy and Institute of Physics (Great Britain), Mott insulators: physics and applications, 2019, <https://iopscience.iop.org/book/978-0-7503-1596-8>.
- 129 X. Sui, J. Wang and W. Duan, *J. Phys. Chem. C*, 2019, **123**, 5003–5009.
- 130 X.-L. Qi and S.-C. Zhang, *Rev. Mod. Phys.*, 2011, **83**, 1057–1110.
- 131 M. Z. Hasan and C. L. Kane, *Rev. Mod. Phys.*, 2010, **82**, 3045–3067.
- 132 M. Fruchart and D. Carpentier, *C. R. Phys.*, 2013, **14**, 779–815.
- 133 H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang and S.-C. Zhang, *Nat. Phys.*, 2009, **5**, 438–442.
- 134 H. Gao, J. W. Venderbos, Y. Kim and A. M. Rappe, *Annu. Rev. Mater. Res.*, 2019, **49**, 153–183.
- 135 X. Zhang, R. Guo, L. Jin, X. Dai and G. Liu, *J. Mater. Chem. C*, 2018, **6**, 575–581.
- 136 M. Hirayama, S. Matsuishi, H. Hosono and S. Murakami, *Phys. Rev. X*, 2018, **8**, 031067.
- 137 H. Huang, K.-H. Jin, S. Zhang and F. Liu, *Nano Lett.*, 2018, **18**, 1972–1977.
- 138 C. L. Kane and E. J. Mele, *Phys. Rev. Lett.*, 2005, **95**, 146802.
- 139 X. Zhang, Z. Xiao, H. Lei, Y. Toda, S. Matsuishi, T. Kamiya, S. Ueda and H. Hosono, *Chem. Mater.*, 2014, **26**, 6638–6643.
- 140 J. Zak, *Phys. Rev. Lett.*, 1989, **62**, 2747–2750.
- 141 X. Zhang, B. Fu, L. Jin, X. Dai, G. Liu and Y. Yao, *J. Phys. Chem. C*, 2019, **123**, 25871–25876.
- 142 K. v. Klitzing, G. Dorda and M. Pepper, *Phys. Rev. Lett.*, 1980, **45**, 494–497.
- 143 M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. W. Molenkamp, X.-L. Qi and S.-C. Zhang, *Science*, 2007, **318**, 766–770.
- 144 C.-Z. Chang, J. Zhang, X. Feng, J. Shen, Z. Zhang, M. Guo, K. Li, Y. Ou, P. Wei, L.-L. Wang, Z.-Q. Ji, Y. Feng, S. Ji, X. Chen, J. Jia, X. Dai, Z. Fang, S.-C. Zhang, K. He, Y. Wang, L. Lu, X.-C. Ma and Q.-K. Xue, *Science*, 2013, **340**, 167–170.
- 145 M. Wu, *2D Mater.*, 2017, **4**, 021014.
- 146 K. Dolui, S. Ray and T. Das, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, **92**, 205133.
- 147 Z. Liu, G. Zhao, B. Liu, Z. F. Wang, J. Yang and F. Liu, *Phys. Rev. Lett.*, 2018, **121**, 246401.
- 148 B. Bradlyn, L. Elcoro, J. Cano, M. G. Vergniory, Z. Wang, C. Felser, M. I. Aroyo and B. A. Bernevig, *Nature*, 2017, **547**, 298–305.
- 149 D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, 1980, **45**, 566–569.
- 150 J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **45**, 13244–13249.
- 151 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.

- 152 L. Hedin, *Phys. Rev.*, 1965, **139**, A796–A823.
- 153 O. G. F. Aryasetiawan, *Rep. Prog. Phys.*, 1998, **61**, 237.
- 154 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207–8215.
- 155 J. Heyd and G. E. Scuseria, *J. Chem. Phys.*, 2004, **121**, 1187–1192.
- 156 A. I. Liechtenstein, V. I. Anisimov and J. Zaanen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1995, **52**, R5467–R5470.
- 157 G. Schulze, *Metallphysik: Ein Lehrbuch*, Springer, Vienna, 2013.
- 158 Y. Lu, T. Tada, Y. Toda, S. Ueda, J. Wu, J. Li, K. Horiba, H. Kumigashira, Y. Zhang and H. Hosono, *Phys. Rev. B*, 2017, **95**, 125117.
- 159 T.-N. Ye, Y. Lu, J. Li, T. Nakao, H. Yang, T. Tada, M. Kitano and H. Hosono, *J. Am. Chem. Soc.*, 2017, **139**, 17089–17097.
- 160 T.-N. Ye, Y. Lu, Z. Xiao, J. Li, T. Nakao, H. Abe, Y. Niwa, M. Kitano, T. Tada and H. Hosono, *Nat. Commun.*, 2019, **10**, 1–10.
- 161 J. Wu, J. Li, Y. Gong, M. Kitano, T. Inoshita and H. Hosono, *Angew. Chem., Int. Ed.*, 2019, **58**, 825–829.
- 162 P. N. H. Nakashima, A. E. Smith, J. Etheridge and B. C. Muddle, *Science*, 2011, **331**, 1583–1586.
- 163 R. Nesper, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 789–817.
- 164 M. E. Eberhart, D. P. Clougherty and J. M. MacLaren, *Philoso. Mag. B*, 1993, **68**, 455–464.
- 165 A. Weiland, J. B. Felder, G. T. McCandless and J. Y. Chan, *Chem. Mater.*, 2020, **32**, 1575–1580.
- 166 E. A. Leon-Escamilla and J. D. Corbett, *Inorg. Chem.*, 2001, **40**, 1226–1233.
- 167 R. Nesper, *Z. Anorg. Allg. Chem.*, 2014, **640**, 2639–2648.
- 168 R. Schäfer and W. Klemm, *Z. Anorg. Allg. Chem.*, 1961, **312**, 214–220.
- 169 S. M. Simon, PhD thesis, University of Wisconsin-Milwaukee, Wisconsin, 2017.
- 170 H. G. v. Schnerring, J. Llanos, J.-H. Chang, K. Peters, E.-M. Peters and R. Nesper, *Z. Kristallogr. - New Cryst. Struct.*, 2005, **220**, 344–346.
- 171 S. G. Dale, A. Otero-de-la Roza and E. R. Johnson, *J. Phys. Chem. C*, 2018, **122**, 12742–12747.
- 172 J. L. Dye, *Science*, 2003, **301**, 607–608.
- 173 J. L. Dye, *Acc. Chem. Res.*, 2009, **42**, 1564–1572.
- 174 A. Walsh, A. A. Sokol, J. Buckeridge, D. O. Scanlon and C. R. A. Catlow, *J. Phys. Chem. Lett.*, 2017, **8**, 2074–2075.
- 175 W. Haynes, *CRC Handbook of Chemistry and Physics*, CRC Press, 2016.
- 176 L. A. Burton and A. Walsh, *J. Solid State Chem.*, 2012, **196**, 157–160.
- 177 L. A. Burton and A. Walsh, *J. Phys. Chem. C*, 2012, **116**, 24262–24267.
- 178 A. Kumar and S. R. Gadre, *Phys. Chem. Chem. Phys.*, 2015, **17**, 15030–15035.
- 179 J.-Y. Raty, M. Schumacher, P. Golub, V. L. Deringer, C. Gatti and M. Wuttig, *Adv. Mater.*, 2019, **31**, 1806280.
- 180 M. Zhu, O. Cojocaru-Mirédin, A. M. Mio, J. Keutgen, M. Küpers, Y. Yu, J.-Y. Cho, R. Dronskowski and M. Wuttig, *Adv. Mater.*, 2018, **30**, 1706735.
- 181 G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.*, 2016, **116**, 2478–2601.
- 182 J. H. de Boer, *Recl. Trav. Chim. Pays-Bas*, 1937, **56**, 301.
- 183 R. P. S. M. Lobo, N. Bontemps, M. I. Bertoni, T. O. Mason, K. R. Poeppelmeier, A. J. Freeman, M. S. Park and J. E. Medvedeva, *J. Phys. Chem. C*, 2015, **119**, 8849–8856.
- 184 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.