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Density-Functional Description of Alkalides: Introducing the Alkalide State

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Alkalides are crystalline salts in which the anion is a negatively charged alkali metal. A systematic investigation of the electronic structure of ten alkalides, with known crystal structures, is conducted using density-functional theory. For each alkalide, a high-lying valence state is identified that is localised on the alkali anions and is consistent with the low band-gap and strong reducing power characteristic of these materials. This 'alkalide state' is compared to a similar state in the related class of electrider materials, where the alkali anions are replaced by crystal voids occupied by localised, interstitial electrons. Finally, a thermodynamic cycle is constructed to examine the energy differences between the alkalides and electrideres, revealing that the alkali-metal anion significantly stabilises the crystal.

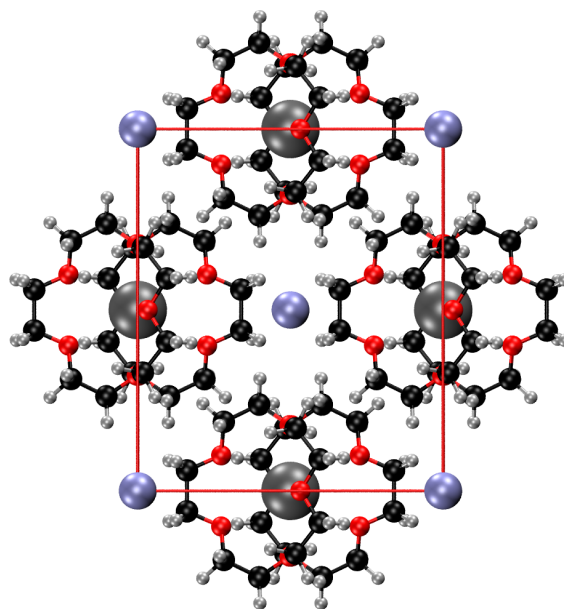
1 Introduction

Alkalides are a class of exotic ionic materials in which alkali metals act as the anions. This unusual chemical structure conveys a number of unique properties, primarily small band gaps (usually between 0.6 and 2.4 eV¹), strong reducing power, and large hyperpolarisabilities. The small band gap in alkalides leaves them in the ambiguous regime between metals and insulators; consequently, they are of considerable interest for study of Mott insulators, and other unusual phenomena in condensed matter physics.^{2,3} To date, the reducing character of the alkalides has seen the most application, particularly after it was discovered that regioselective reactivity is possible for C-O bond cleavage.⁴⁻¹¹ This subsequently led to the examination of alkalides as potential reagents for polymerisation initiation,¹²⁻¹⁶ as well as other applications requiring potent reducing agents.¹⁷⁻²⁷ Further, synthesis of metal nanoparticles via alkalide reduction is an increasingly common practice, as it provides a fast, quantitative preparation at low temperatures.²⁸⁻³⁹ However, the tendency of alkalide anions to attack C-O bonds leads to the decomposition of the complexing ligands that form the organometallic framework of the alkalide crystals.⁴⁰⁻⁴³ Consequently, the majority of alkalides are unstable at room temperature and when exposed to atmospheric conditions.

The unit cell of a typical alkalide, Cs⁺(15C5)₂K⁻, is shown in Figure 1. The *mCn* notation is used throughout this work to represent crown ethers with formula *m*-crown-*n*. Alkalides consist

of an alkali metal cation complexed to one or more organic ligand(s); in this case Cs⁺ is complexed to two 15C5 molecules. This stabilises the cation and destabilises the 6s electron so much that reduction of a neighbouring uncomplexed alkali atom, in this case K, is energetically favourable. The presence of both alkali cations and anions in the alkalide materials has been confirmed using NMR spectroscopy.^{1,44-51} A list of all the known, synthesised organic alkalide crystals is provided in Table 1.

Fig. 1 The unit cell of Cs⁺(15C5)₂K⁻. The Cs cations are represented by larger, grey spheres at the centre of the 15C5 cages, and the K anions by blue spheres at the vertices and centre of the unit cell.



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In recent years, computational studies of molecular alkalides have been reported.^{52–71} Molecular alkalides consist of pairs of alkali metal atoms that are complexed to a ligand that stabilises an alkali cation and forces the highest valence electron into an extremely diffuse state centered about the other alkali atom. These molecules demonstrate remarkable hyperpolarisabilities, but to date remain purely theoretical constructs and will not be considered in this work.

No prior computational or theoretical description of the known alkalide crystals has, to the authors' knowledge, been published. This work seeks to remedy this, and will focus on a selection of known alkalides with the goal of understanding their electronic structure in greater detail.

To begin, we draw comparisons to previous computational investigations of electrides. Electrides are similarly unique ionic crystals in which the anion is stoichiometrically replaced with a localised electron. Alkalides and electrides can be synthesised using practically identical methods, possess many of the same properties, and (with the exception of the alkali anion) have almost identical chemical compositions. Indeed the simplest electride has the chemical formula $\text{Cs}^+(15\text{C}5)_2\text{e}^-$, analogous to the $\text{Cs}^+(15\text{C}5)_2\text{K}^-$ alkalide shown in Figure 1. However, in contrast to the alkalides, the electrides have been the subject of thorough theoretical investigation.

Most of the early theoretical work on electrides focused on verifying the presence of the localised interstitial electron,^{72–78} as it cannot be observed using current experimental techniques. More recent theoretical studies have examined the electronic structure^{2,79–91} and magnetic behaviour^{3,92,93} of the electrides, as well as proposing new electride materials.^{94–102} Of particular relevance to the present work, a 1993 paper by Singh *et al.* used density-functional theory to examine the electride, $\text{Cs}^+(15\text{C}5)_2\text{e}^-$.⁷⁶ The band structure revealed a high-energy valence state, coined the 'electride state', with electron density primarily localised within the crystal voids. This state is the source of a number of the electride's characteristic properties, such as the extremely low band gap. In 2014, this study was expanded, identifying an equivalent state for all of the known organic electrides.⁸⁸

In the present work, we demonstrate that a corresponding high-lying valence state exists for the alkalide crystals. This 'alkalide state' is primarily localised on the negatively charged alkali-metal atoms and is similarly responsible for the unique alkalide properties, highlighting the close link between the alkalide and electride materials. Finally, we employ a thermodynamic cycle to show that the presence of the alkali anion significantly stabilises the crystal lattice, partly through increased London dispersion forces, explaining the greater observed stability of the alkalides relative to the electrides.

2 Computational Methods

All calculations on the studied alkalides used initial geometries taken from the experimental crystal structures in the Cambridge Structural Database (CSD).¹⁰³ Minor modifications were made to some of these structures to correct obvious errors; for example, $\text{Rb}^+(\text{C}222)\text{Rb}^-$ (JAPVIF) was missing 4 hydrogen atoms. The

atomic positions were then allowed to relax, while keeping the cell parameters fixed. This allowed the hydrogen atoms to move into energetically stable positions as they are usually algorithmically placed upon determination of the heavy-atom locations within a crystal structure. We have previously found that geometric relaxation of the crown-ether molecules allows greater stabilisation of electrides, leading to increased negative charge on the complexing ligands,⁸⁸ and we expect a similar phenomenon to occur in this work. The alkalides for which calculations were conducted were chosen primarily for their smaller unit cell size, for computational efficiency, and for chemical simplicity to aid interpretation. Table 1 provides a list of all the experimentally synthesised alkalide crystals. Alkalide crystals for which calculations were conducted are labelled with an (*) and listed again in Table 2. Note that some of the reported alkalide crystals possess significant structural errors; calculations on these species, even with minor geometry modifications, were not possible. These alkalides are labelled with a (†) in Table 1.

All computations used the PBE¹⁰⁴ functional, together with the exchange-hole dipole moment (XDM)^{105,106} model to ensure accurate treatment of dispersion forces. The calculations were conducted under periodic boundary conditions using the Quantum ESPRESSO¹⁰⁷ package, with a 50 Ry planewave cut-off energy, a 500 Ry density cut-off, and a cold-smearing¹⁰⁸ temperature of 0.01 Ry. The Projected Augmented Wave (PAW) formalism¹⁰⁹ was employed with pseudopotentials adapted from the atompaw library.¹¹⁰ The number of *k*-points used for each alkalide is listed in Table 2 and varied depending on the unit cell size.

3 Characterisation of the Alkalide State

The computed band structures of the alkalides studied here are shown in Figure 2. In all cases, the band structure reveals a valence state immediately below the Fermi level, energetically separated from the rest of the valence band and usually within 1 eV of the conduction band. This state is clearly responsible for the small band gaps observed for the alkalide materials. For the purpose of discussion we will call this high-lying state the 'alkalide state'. The density of this state is plotted for each considered alkalide in Figure 3. For each crystal, the valence density is centered on the alkali metal that is not bound to complexing ligands, giving rise to its anionic character.

Table 1 List of the synthesised alkali crystals, the first literature reference to each crystal, the CSD ¹⁰³ code (where available), and number of atoms in each unit cell. Efforts have been made to remain consistent with the notation used in the original publications, with minor alterations for consistency. Abbreviations for complexing ligands are given below the table.

CSD Code	Formula	Total Atoms per unit cell	Source
REGCAH*	K ⁺ (12C4) ₂ Na ⁻	232	111
FABMEA10*	Rb ⁺ (15C5) ₂ Na ⁻	144	112
JEPMIA*	Rb ⁺ (15C5) ₂ Rb ⁻	144	113
PEZRIV†	Cs ⁺ (15C5) ₂ Na ⁻	-	114
JEPMEW*	Cs ⁺ (15C5) ₂ K ⁻	144	113
JAPVOL*	Rb ⁺ (18C6)Rb ⁻	176	115
COBNEW†	Cs ⁺ (18C6)Na ⁻	-	116
REGCIP*	[Rb ⁺ (18C6)Na ⁻](CH ₃ NH ₂)	204	111
REGDEM†	[K ⁺ (18C6)Na ⁻](CH ₃ NH ₂) ₂ (18C6) ₃	636	111
FUJCUI	Cs ⁺ (18C6) ₂ Cs ⁻	688	117
FABMAW10*	Cs ⁺ (18C6) ₂ Na ⁻	344	112
COJDIO*	Li ⁺ (18C6)(CH ₃ NH ₂) ₂ Na ⁻	232	118
COJFAI†	[Li ⁺ (18C6)(CH ₃ NH ₂) ₂ Na ⁻](18C6)	180	118
PEZRER†	Cs ⁺ (18C6)(15C5)Na ⁻	-	114
PEZPAL†	K ⁺ (18C6)(12C4)Na ⁻	264	114
PEZPEP†	K ⁺ (18C6)(12C4)K ⁻	248	114
PEZPIT	[K ⁺ (18C6)(12C4)K ⁻](18C6)	456	114
FABMEA01†	Rb ⁺ (18C6)(12C4)Na ⁻	280	114
JEPMIB†	Rb ⁺ (18C6)(12C4)Rb ⁻	272	114
CRYPNA10†	Na ⁺ (C222)Na ⁻	-	119
TAFLAN†	K ⁺ (C222)Na ⁻	512	120
JAPVEB*	K ⁺ (C222)K ⁻	128	115
JAPVIF*	Rb ⁺ (C222)Rb ⁻	128	115
FUJDAP*	Cs ⁺ (C222)Cs ⁻	256	117
REJBAK*	Li ⁺ (C211)Cs ⁻	200	121
ROGDEW*	Li ⁺ (C211)Na ⁻	200	122
REGCEL	Na ⁺ (C221)Na ⁻	228	111
REGVUU	Cs ⁺ (C322)Na ⁻	284	111
-	K ⁺ (aza222)Na ⁻	-	123
-	K ⁺ (aza222)K ⁻	-	123
HAGNOT	Ba ²⁺ (H ₅ aza222 ⁻)Na ⁻ (CH ₃ NH ₂) ₂	544	124
DAWCEK	Na ⁺ (TriPip222)Na ⁻	328	96
-	K ⁺ (HMHCY)Na ⁻	-	125
-	Cs ⁺ (HMHCY)Na ⁻	-	125
TOJFAZ	Li ⁺ (TMTCY)[Li ⁺ (DMTCY ⁻).(CH ₃ NH)]Na ⁻	232	126
COHZAA	Li ₂ ⁺ (TMTCY) ₂ .(CH ₃ NH ⁻)Na ⁻	576	118
REGXAC	[Li ₂ ⁺ (TMPAND) ₂ Na ₂ ⁻](CH ₃ NH ₂)	248	111
-	Li ⁺ (TMPAND) ₂ Na ⁻	-	127

mCn: a crown ether containing n oxygen atoms and m total heavy atoms

Cxyz: a cryptand with x, y, and z oxygen atoms on each arm of the cage

aza: a fully methylated nitrogen-cryptand analogue

TriPip222: 1,4,7,10,13,16,21,24-octaazapentacyclo[8.8.8.24,7.213,16.221,24]dotriacontane

HMHCY: hexamethyl hexacyclen, the fully methylated nitrogen analogue of 18-crown-6

TMPAND: 5,12,17-trimethyl-1,5,9,12,17-pentaaulbicyclo[7.5.5]nonadecane

TMTCY: trimethyl tricyclen (1,4,7-trimethyl-1,4,7-triazacyclononane)

DMTCY: dimethyl tricyclen (1,4-dimethyl-1,4,7-triazacyclononane)

Fig. 2 Band structure and corresponding density of states (DOS) of selected alkalides. The band structure plots show energies (in eV) of each band along the specified k -path. DOS plots show the total DOS in blue and the DOS of the negatively charged alkali metal atoms in red.

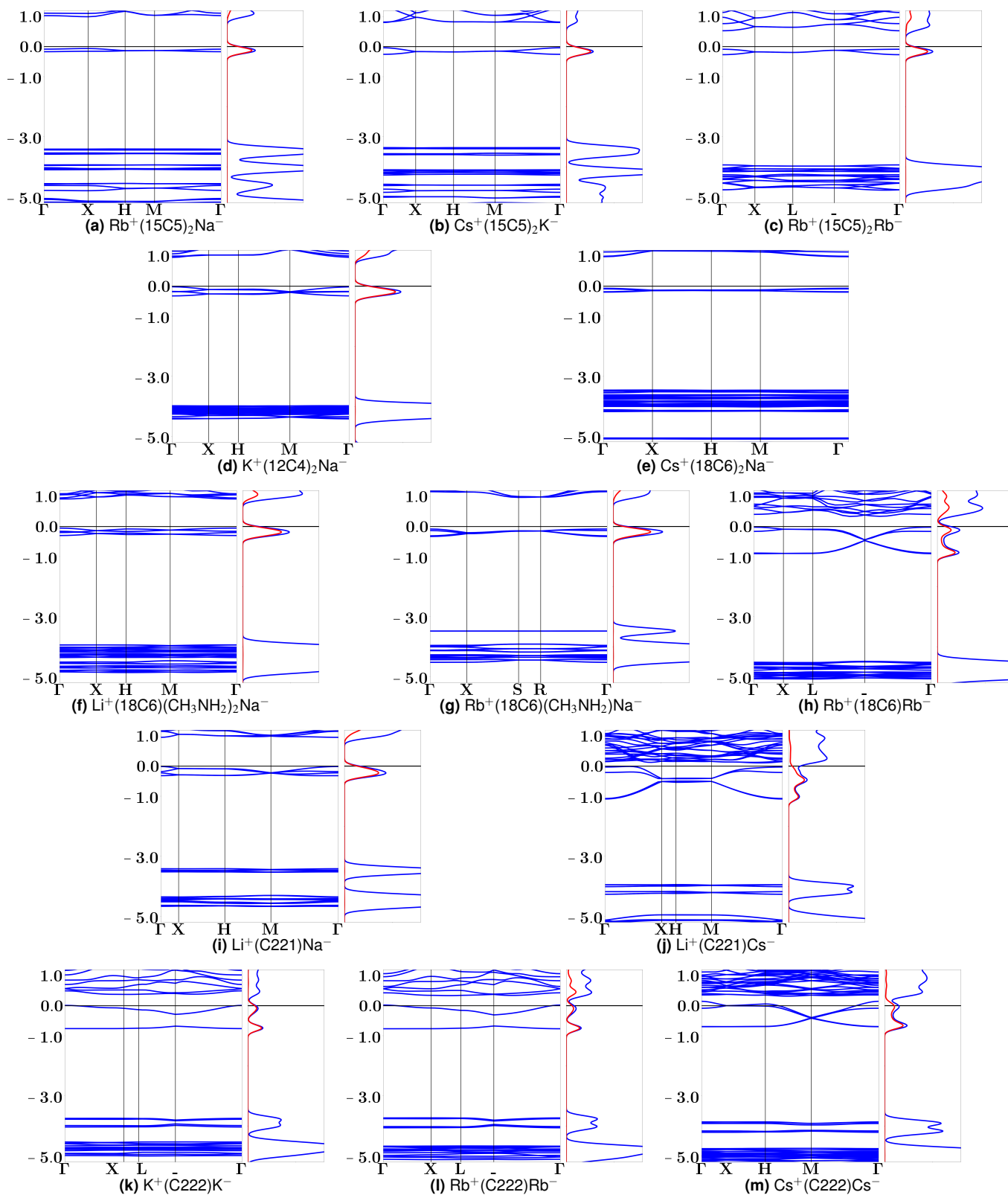


Fig. 3 Valence-band densities of selected alkali crystals, plotted using a 0.0015 a.u. isosurface for all except $\text{Li}^+(\text{C221})\text{Cs}^-$ and $\text{Cs}^+(\text{C222})\text{Cs}^-$, for which a 0.0010 a.u. isosurface was used.

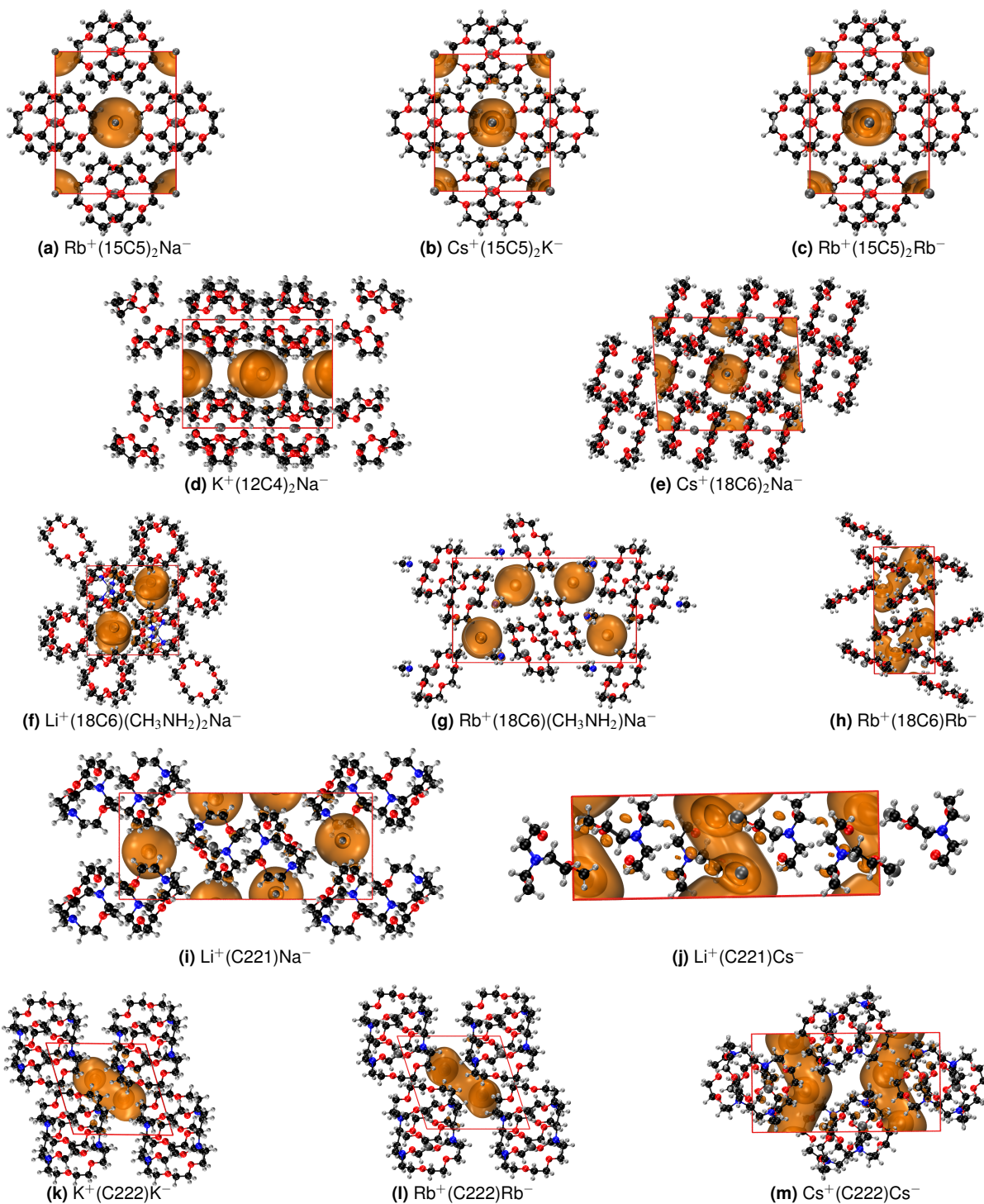


Table 2 gives atomic charges for the alkali cation and anion within each alkalide crystal, evaluated using Bader's quantum theory of atoms in molecules (QTAIM).^{128–131} The charges were computed from the PBE electron densities, using the Yu-Trinkle algorithm,¹³² as implemented in the Critic2 program.¹³³ The results reveal near-integer positive charges on the alkali cations and a consistently negative, fractional charge for the alkali anions. The fractional negative charge implies that the alkalide state is extremely diffuse, overlapping with the neighbouring organic molecules. The appearance of fractional charges for both the cations and anions is exacerbated by the delocalisation error inherent in the density-functional method used.^{134–143} Indeed, were this error to be eliminated, we would expect the localised charge to increase in each case. Unfortunately, mitigating this error is often extremely computationally expensive and is impractical in the present work.^{142,144}

The density-of-states (DOS) for each alkalide is also provided in Figure 2. In each case the total DOS and DOS of the anionic alkali metal is plotted. The anionic alkali metal atom identity is determined using QTAIM charges and is always consistent with the localisation of the valence density plotted in Figure 3. The DOS plots reveal the primary contribution to the alkalide state is indeed the anionic alkali metal.

4 Comparison to the Electrides

Comparison of the results presented for the alkalides to equivalent data for the electrides reveals a number of similarities. As was highlighted in Section 1, the electrides possess a high-lying valence state, first identified for a single electride in 1993⁷⁶ and for the remaining electrides in 2014.⁸⁸ This is similar to the 'alkalide state' identified in Figure 2. Valence-density plots reveal that the electride state is primarily localised within the crystal voids. These are geometrically equivalent to the positions of the alkali metal anions, on which the alkalide state is localised, as shown in Figure 3.

In some cases, the alkalide state in the band structure spans almost an electron volt and the corresponding valence density is not spherically symmetric about the alkali anion, forming channels through the crystal. This typically occurs when a heavier alkali metal is negatively charged (as for $\text{Rb}^+(\text{18C6})\text{Rb}^-$, $\text{Rb}^+(\text{C222})\text{Rb}^-$, $\text{Li}^+(\text{C221})\text{Cs}^-$, and $\text{Cs}^+(\text{C222})\text{Cs}^-$), although this is not always the case ($\text{K}^+(\text{C222})\text{K}^-$ is an exception). This result is reminiscent of the valence density for the $\text{K}^+(\text{C222})\text{e}^-$ electride, known to display 2D localised-electron coupling through analogous crystal channels.^{3,88} We propose that the heavier atoms allow for a broader spatial distribution of the alkalide state. This provides the potential for pseudo bonding and anti-bonding between neighbouring anionic species within alkalide crystal, and hence the two distinct alkalide states identified in the DOS. The potential for overlap is also affected by the crystal packing motif, dictated by the ligand molecules. In cases where such overlap is possible, it allows for significant polarisation of the valence density through channels within the crystal lattice.

The atomic charges in Table 2 reveal almost complete ionisation of the complexed alkali cation, in agreement with equivalent calculations for the electride crystals.¹⁴⁵ Further, the frac-

tional negative charges localised on each alkali anion are consistent with the fractional negative charges localised within the crystal voids for the electrides.^{88,93} This implies that the negative charge is very diffuse, overlapping with, and stabilised by, the neighbouring organic ligands. We do note that the amount of localised charge is typically higher for the alkalides than for the electrides. For the un-relaxed crystal geometries of the electrides, the QTAIM charges for the non-nuclear maxima ranged from -0.132 to $-0.361 e^-$.⁸⁸ Here, the QTAIM charges for the alkalide anions at the un-relaxed crystal geometries (reported in Table 1 of the Supplementary Information†) range between -0.264 and $-0.472 e^-$.

Comparing the anion charges for the un-relaxed crystal geometries from the CSD (given in Table 1 of the Supplementary Information†) to equivalent charges for the relaxed alkalide crystal geometries (presented in Table 2) reveals significant changes upon relaxation. The most egregious example is $\text{Cs}^+(\text{15C5})_2\text{K}^-$, for which the K^- charge decreased in magnitude from $-0.413 e^-$ to $-0.111 e^-$ upon relaxation. The average decrease in the magnitude of the negative charge is $\sim 0.15 e^-$ for the other alkalide crystals. This is consistent with our recent work, which examined $\text{Cs}^+(\text{15C5})_2\text{e}^-$ under pressure. Calculations on $\text{Cs}^+(\text{15C5})_2\text{e}^-$ at literature and relaxed geometries yielded non-nuclear-maximum charges of $-0.361 e^-$ ⁸⁸ and $-0.25 e^-$,¹⁴⁵ respectively. Geometric relaxation of the complexing ligands enables better charge stabilisation, decreasing the magnitude of the localised charge at either the alkalide-anion or crystal-void site. The fractional negative charges are further consistent with the interpretation that the alkalide and electride states are extremely diffuse.

5 Thermodynamic Cycles

The alkalide crystal structures $\text{Cs}^+(\text{15C5})_2\text{K}^-$ and $\text{Cs}^+(\text{18C6})_2\text{Na}^-$ are nearly identical to the electride crystal structures $\text{Cs}^+(\text{15C5})_2\text{e}^-$ and $\text{Cs}^+(\text{18C6})_2\text{e}^-$, accounting for the absence of K and Na, respectively. This provides an opportunity to compare the relative stabilities of the alkalide crystals with respect to their electride counterparts. Figures 4 and 5 present thermodynamic cycles for removal of the K and Na atoms from $\text{Cs}^+(\text{15C5})_2\text{K}^-$ and $\text{Cs}^+(\text{18C6})_2\text{Na}^-$, respectively. In each case the alkalide crystal geometry is held fixed upon removal of the relevant alkali metal atom, followed by relaxation of the resulting electride structure.

From Figures 4 and 5, the alkalides are more stable than the electrides, by 0.61 eV and 1.66 eV for $\text{Cs}^+(\text{15C5})_2\text{K}^-$ and $\text{Cs}^+(\text{18C6})_2\text{Na}^-$, respectively. A significant portion of these energy differences (viz. 0.22 eV and 0.29 eV, respectively) arises from the XDM dispersion contribution of the alkali metal anion to the lattice energy. Further, after removal of the alkali atoms, the volume of the electride unit cells decreases significantly, from 5657 to 4947 bohr³/cation for $\text{Cs}^+(\text{15C5})_2(\text{K/e})^-$ and from 6254 to 6060 bohr³/cation for $\text{Cs}^+(\text{18C6})_2(\text{Na/e})^-$. This suggests that an essential role of the alkali anion in alkalide formation is simply providing a framework around which the alkali metal-ligand complexes can stack and stabilise.

The significant difference in the stabilisation energy between the two thermodynamic cycles is a consequence of the crystal

Table 2 List of the alkalide crystals for which calculations were conducted in this work and the k -point mesh used. QAIM atomic charges for the alkali cations and anions, and atomic volumes for the alkali anions (in atomic units), are also given.

CSD Code	Formula	k -points ($k \times k \times k$)	Alkali Charge	Alkalide Charge	Alkalide Volume (bohr ³)
REGCIP	Rb ⁺ (18C6)(CH ₃ NH ₂)Na ⁻	2	0.844	-0.274	517.6
FABMEA10	Rb ⁺ (15C5) ₂ Na ⁻	4	0.904	-0.295	560.3
ROGDEW	Li ⁺ (C211)Na ⁻	2	0.895	-0.338	588.2
COJDIO	Li ⁺ (18C6)(CH ₃ NH ₂) ₂ Na ⁻	2	0.888	-0.340	590.9
REGCAH	K ⁺ (12C4) ₂ Na ⁻	2	0.876	-0.325	602.2
FABMAW10	Cs ⁺ (18C6) ₂ Na ⁻	2	0.921	-0.331	615.1
JEPMEW	Cs ⁺ (15C5) ₂ K ⁻	4	0.913	-0.111	695.7
JAPVEB	K ⁺ (C222)K ⁻	4	0.874	-0.244	780.8
JEPMIA	Rb ⁺ (15C5) ₂ Rb ⁻	4	0.904	-0.100	771.2
JAPVOL	Rb ⁺ (18C6)Rb ⁻	2	0.737	-0.277	805.8
JAPVIF	Rb ⁺ (C222)Rb ⁻	4	0.870	-0.206	825.1
FUJDAP	Cs ⁺ (C222)Cs ⁻	2	0.873	-0.187	1007.6
REJBAK	Li ⁺ (C211)Cs ⁻	2	0.891	-0.220	1052.7

packing. The similarity between the alkalide and electride crystal structures can be quantified using the critic2 program¹³³ by evaluating the overlap of the calculated powder diffraction spectra. A POWDIFF value of zero indicates identical structures, while a value of one indicates maximal dissimilarity.^{146,147} The Cs⁺(18C6)₂Na⁻ alkalide and Cs⁺(18C6)₂e⁻ electride share the same C2/c space group^{112,148} and the resulting POWDIFF of only 0.042 implies that the crystal structures are extremely similar. This is reflected by the 0.04 eV relaxation energy for the electride in Figure 5. Conversely, the Cs⁺(15C5)₂K⁻ alkalide (space group C2/m¹¹³) and the Cs⁺(15C5)₂e⁻ electride (space group P-1¹¹³) have significantly different structures, with a POWDIFF of 0.320. The change in symmetry on relaxation of Cs⁺(15C5)₂e⁻ allows for a more favourable atomic arrangement, leading to the 0.90 eV energy difference in Figure 4.

The increased stability of the alkalide crystals, relative to the electrides, helps explain the differing rates of development of the two fields over the past three decades. The alkali anion provides additional stability to the alkalide crystals, making them easier to produce and slightly less susceptible to decomposition. In light of this, it is hardly surprising that alkalides were discovered first, in 1974,⁴⁴ with currently 38 known, synthesised examples. In contrast, only 7 known organic electrides have been synthesized since their discovery in 1983.¹⁴⁹

6 Conclusions

In this work, we have systematically examined the band structures of ten alkalides with known crystal structures. All of the calculated band structures reveal a high-lying valence state, which corresponds to densities primarily localised on the alkali metal anion within each alkalide. This ‘alkalide state’ confers a number of desirable properties to the alkalide materials, most notably low band gaps and strong reducing power. The alkalide state compares well to an equivalent electride state in the related electride materials. A thermodynamic cycle was constructed for two iso-structural alkalide/electride crystal pairs. The alkali metal anion was shown to provide increased stability to the alkalide crystal

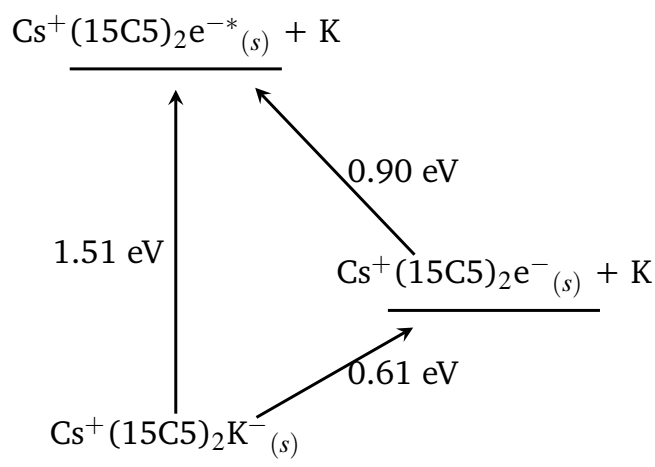


Fig. 4 A thermodynamic cycle for removal of K from the Cs⁺(15C5)₂K⁻ alkalide, followed by relaxation of the crystal structure to its electride equivalent, Cs⁺(15C5)₂e⁻. Energies are reported per Cs⁺ cation. Cs⁺(15C5)₂e^{-*} is iso-structural to Cs⁺(15C5)₂K⁻ with the exception of the K atoms.

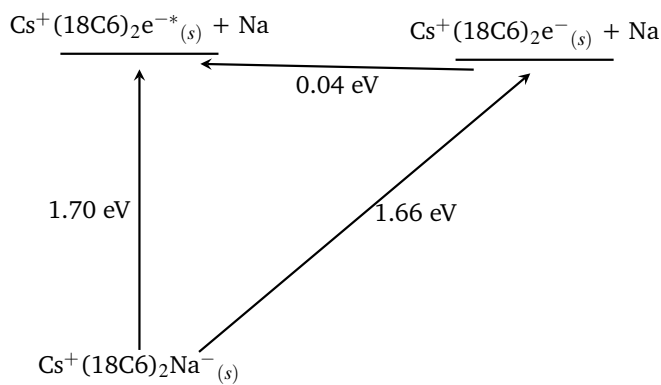


Fig. 5 A thermodynamic cycle for removal of Na from the Cs⁺(18C6)₂Na⁻ alkalide, followed by relaxation of the crystal structure to its electride equivalent, Cs⁺(18C6)₂e⁻. Energies are reported per Cs⁺ cation. Cs⁺(18C6)₂e^{-*} is iso-structural to Cs⁺(18C6)₂Na⁻ with the exception of the Na atoms.

over the electricle crystal.

The electricle field has seen significant advances in recent years, in part due to numerous theoretical and computational studies. We expect a deeper understanding of the electronic structure and properties of the alkalides, in conjunction with the many shared links between the alkalides and electricle, to aid continuing efforts in both fields.

7 Conflicts of Interest

There are no conflicts of interest.

8 Acknowledgements

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