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1. Introduction

As the most versatile light metals, aluminum (Al) and magnesium (Mg) are considered to approach an "ideal" metal or freeelectron gas where electrons move freely without being affected by the metal ions. However, their electronic behaviors are drastically different under high pressure. Specifically, the electron density in the tetrahedral interstitial sites of fcc-Al is found to be in excess of the superposition of the unbound atoms' free electrons under high pressure.^{1,2} Electron localization in the interstitial sites of Al is even more pronounced above the terapascal (TPa) range.³ Similar to Al, the valence electrons of the fcc and sh structures of Mg are also found to be localized in the interstitial regions.⁴ Therefore, the electrons of these two metals are confined in the cavities or channels of the lattice under high pressure, forming the so-called electrides.^{5,6}

An electride can be defined as a peculiar ionic compound where some electrons in the solid are localized at interstitial regions, rather than being bound to any particular nucleus.^{5,7,8} In addition, the formation of electrides becomes more energetically favorable under high pressure.^{9,10} The hallmark feature of electrides is the formation of off-center lobes of electrons, also known as "quasi" atoms⁹ or nuclear attractors (NNAs).¹¹ To date, various electrides have already been found to be induced by pressure both in elements and compounds mainly including alkali and alkaline earth elements, such as K,¹² Na,¹³

Predicted stable electrides in Mg–Al systems under high pressure†

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Magnesium and aluminum, as adjacent light metal elements, have difficulty forming stable stoichiometric compounds under ambient conditions. In this work, using evolutionary *ab initio* structural prediction approaches, we have systematically explored the entire compositional space to identify possible stoichiometries of Mg–Al compounds at pressures of up to 100 GPa. Here, three compounds, Mg₃Al, MgAl and MgAl₃, are predicted to be thermodynamically stable at certain pressure conditions. In particular, we discovered that these newly found compounds are essentially electrides with excess electrons confined in the interstitial voids, which is attributed to the 3p orbitals of the two nearest-neighbor Al atoms overlapping under high pressure. This work will provide an avenue for further experimental study of the new structures of Mg–Al systems, and will also have far-reaching implications on the understanding of materials chemistry under high pressure.

Li,¹⁴ Ca,¹⁵ Na₂He,¹⁶ Li₆P¹⁷ and Mg₂O₃,¹⁸ which often possess unusual physical properties. In fact, research on electrides has been a recurring theme in the literature.^{19–28}

Considering that interstitial electrons exist in Al^{2,3} and Mg⁴ elements as well as some of their binary compounds^{18,22,29,30} and that the mixed materials of Mg and Al are electron-rich systems, Mg-Al compounds have considerable potential to be good candidates for electrides under high pressure. At ambient pressure, three intermetallics (γ -Mg₁₂Al₁₇, β -Mg₃Al₂ and ε-MgAl) are found in the equilibrium Mg–Al phase diagram,³¹ which all exhibit off-stoichiometric compositions. Although Mg and Al have difficulty forming stoichiometric compounds at ambient conditions, it could be overcome by reducing the formation energy barriers under high pressure to form chemically stable compounds. In this context, we switch our focus to high-pressure conditions. We systematically searched the crystal structures of different stoichiometric Mg-Al systems in a pressure range of 0 to 100 GPa. Three stoichiometric compounds, Mg₃Al, MgAl and MgAl₃, are verified to be thermodynamically stable at certain pressure conditions. More importantly, our calculations reveal that these new compounds are potential electrides, which is attributed to an overlap of the 3p orbitals of the two nearest-neighbor Al atoms.

2. Computational details

The search for the stable stoichiometric compounds of Mg–Al alloys under pressure was carried out by the global minimization of free energy surfaces by *ab initio* total energy calculations as implemented in the CALYPSO^{32,33} code with the particle

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Paper

swarm optimization (PSO) algorithm. This methodology has successfully been used to predict various compounds.³⁴⁻³⁷ Structural optimization and electronic property calculations were performed in the framework of density functional theory (DFT) within the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA_PBE)³⁸ as implemented in the VASP code.³⁹ The electron-ion interaction is described by pseudopotentials built within the projector augmented wave (PAW)⁴⁰ method with 2p63s2 valence electrons for Mg and 3s23p1 valence electrons for Al. A cutoff energy of 800 eV and Monkhorst–Pack *k* meshes⁴¹ with a grid spacing of $2\pi \times 0.015$ Å⁻¹ were used to yield a good convergence for the enthalpy ($\Delta H <$ 1 meV per atom). The pseudopotential and exchangecorrelation functions were tested for validation (Fig. S1, ESI[†]). To ensure the dynamical stability of the predicted compounds, the phonon spectra were calculated with the supercell method as implemented in the PHONONPY code.42 The transferred charges were calculated by Bader's quantum theory of atom-inmolecules (QTAIM) analysis⁴³ and the electron localization function (ELF)⁴⁴ for all compounds. The mechanical properties were calculated based on linear response theory⁴⁵ as implemented by VASP.38 Detailed descriptions of the computational approaches can be found in the ESI.[†]

3. Results and discussions

An extensive search for the crystal structures of Mg_xAl_{1-x} (0.2 $\leq x \leq$ 0.8) binary compounds was performed at 0 GPa, 20 GPa, 40 GPa, 60 GPa and 100 GPa with maximum simulation cells of up to 4 formula units (f.u.) for each fixed composition. The thermodynamic stabilities of the Mg–Al system with different stoichiometries were systematically investigated by calculating the formation enthalpies relative to Mg and Al at the corresponding pressure. We calculated the enthalpy of formation per atom using the following formula:

$$\Delta H^{\mathrm{I}}(\mathrm{Mg}_{x}\mathrm{Al}_{y}) = [H(\mathrm{Mg}_{x}\mathrm{Al}_{y}) - xH(\mathrm{Mg}) - yH(\mathrm{Al})]/(x+y)$$

where the enthalpies *H* for Mg_xAl_y , Mg and Al are obtained for the most stable structures at the desired pressures. For Al, it is well known that the FCC structure can be stable up to 200 GPa.^{46,47} For Mg, with increasing pressure, the known structure HCP (*P*63/*mmc*) transforms into BCC ($Im\bar{3}m$) at 45 GPa.^{48,49} The convex hulls under different pressures are summarized in Fig. 1(a). To have a better comparison, the formation energies of already existing structures in the Materials Project⁵⁰ database under ambient pressure are also provided in the convex hull. The compounds located on the convex hull are stable, whereas compounds lying on the dotted lines are metastable.

From the convex hull, we found that only the MgAl compound is thermodynamically stable under ambient pressure. The off-stoichiometric compounds γ -Mg₁₇Al₁₂ and ϵ -Mg₃Al₂ are located above the convex hull, indicating their thermodynamic instability under ambient pressure. Under further compression, it can be seen that MgAl₃ and Mg₃Al compounds gradually stabilize. When the pressure is above 60 GPa, Mg₃Al becomes



Fig. 1 Relative thermodynamic stability of Mg_xAl_y at 0 K and different pressures (0, 20, 40, 60 and 100 GPa). (a) The convex hull of Mg_xAl_y compounds. The thermodynamically stable and metastable compounds are shown using solid symbols connected by a solid line and open symbols connected by a dotted line, respectively. The half-full diamonds represent the formation energy adopted from Material Project.⁵⁰ (b) Pressure–composition phase diagram of Mg_xAl_y compounds.

the most stable compound. Meanwhile, the shift of the phase stability towards Mg compositions is accompanied by some structural changes as the pressure increases. The pressure–composition phase diagram is shown in Fig. 1(b). The enthalpies per atom of all phases predicted are shown in the Fig. S2, ESI.†

Under ambient pressure, our simulations show that the MgAl stoichiometric compound stabilizes into a tetragonal



Fig. 2 Crystal structures of the stable Mg–Al compounds. (a) P4/mmm MgAl, (b) Pmmb MgAl, (c) $Pm\overline{3}m$ MgAl₃, (d) P63/mmc MgAl₃, (e) P63/mmc Mg₃Al and (f) $Fm\overline{3}m$ Mg₃Al. In all these structures, blue and orange spheres represent Mg and Al atoms, respectively.

structure (Fig. 2(a)) with a space group symmetry of P4/mmm, which is consistent with the structure from Materials Project.⁵⁰ The P4/mmm structure is composed of one Mg atom occupying the 1b site and one Al atom occupying the 1c site, in which each Al has eightfold coordination. At a pressure above 40.5 GPa, we discovered that the orthorhombic Pmmb structure of MgAl becomes more thermodynamically stable. As depicted in Fig. 2(b), this high-pressure structure has also one Mg atom occupying the 2f site and one Al atom occupying the 2e site. The coordination numbers of Al are also eightfold. In the other components, only MgAl₃ and Mg₃Al compounds were predicted to be stable. When the pressure is above 20 GPa, the cubic $Pm\bar{3}m$ structure of MgAl₃ shown in Fig. 2(c) (Mg in the 1a site, Al in the 3c site) is stable up to 90.8 GPa, then transfers to an orthorhombic P63/mmc phase (Fig. 2(d), Mg in the 2d site, Al in the 6h site). Al atoms in $Pm\bar{3}m$ MgAl₃ and P63/mmc MgAl₃ coordinate with 4 Mg atoms. As for Mg₃Al, it is stable in an orthorhombic structure (Fig. 2(e)) with the P63/mmc space group (Mg in the 4c and 8g sites, Al in the 4c site) above 45 GPa and transfers to cubic $Fm\bar{3}m$ (Fig. 2(f), Mg in the 8c and 4b sites, Al in the 4a site) under 64.4 GPa. 12-Fold and 8-fold coordinations of Al atoms are observed in P63/mmc and Fm3m MgAl₃, respectively. More details about the structural information can be found in the Table S1, ESI.†

To access the dynamical stability of these newly predicted compounds, we used the supercell method to calculate their phonon spectra. All of their phonon spectra do not show any imaginary modes in their stability pressure ranges, indicating their dynamic stability (Fig. 3(a–f)). Furthermore, the elastic constants and moduli were calculated to verify the mechanical stability of our predicted structures. Under certain stable pressures, the elastic constants and moduli of our predicted structures are shown in Table 1, which all meet the mechanical stability criteria.⁵¹ Therefore, these predicted structures are mechanically stable (the formulas for calculating the elastic moduli and the mechanical stability criteria can be found in the ESI[†]).

We now explore the so far undiscovered stoichiometric compounds by a series of first-principles calculations on their electronic structures. The electronic band structures and the corresponding projected density of states (PDOS) are plotted in Fig. 4. It is seen that all these structures show metallic features. Note that, the conducting states mainly come from Al-3p states around the Fermi level. With the composition of Mg increasing, the Mg-3p states exhibit more contribution to the states near the Fermi level. Furthermore, we found some flat bands appearing in these band structures, e.g. $\Gamma \rightarrow A (-6 \text{ to } -4 \text{ eV})$ in DOS) in P63/mmc MgAl₃. According to the nearly free electron model (NFE), the parabolic-like dispersions of metal can be perturbed by localized electrons.⁵² Thus, one might expect that the flat bands of P63/mmc MgAl₃ are mainly caused by the localized electrons in the interstitial sites, which is further supported by our Bader charge calculations results. The electron counts of these different stoichiometries are shown in Table 2 (including total and transferred charges for each ion). Excess electrons clearly accommodate into the interstitials of the lattice in four compounds ($Pm\bar{3}m$ MgAl₃, P63/mmc MgAl₃, Pmmb MgAl and P63/mmc Mg₃Al), which indicates the formation of electrides.

In these potential electrides, we take the P63/mmc phase of MgAl₃ as a typical example. We performed certain calculations to analyze the electronic properties, which will be discussed below. In order to better understand the interstitial electrons, the electronic structure of the most stable P63/mmc MgAl₃ phase at high pressures was analyzed by Bader charge analysis and ELF. The calculated ELF in Fig. 5(a) of P63/mmc MgAl₃ under 100 GPa characterizes that the localization of excess electrons is in the interstitial cavities of the lattice, forming a pseudo-atom-like entity. Moreover, using the Bader charge analysis, we found that the excess electrons could be partitioned into (based on the zero-flux surface of the charge density) a volume separating them from the atoms. These offatom electron lobes (or NNAs) are further confirmed by the partial charge density, as seen in Fig. 5(b). To quantitatively demonstrate the location of the off-atom electrons, we integrated the electrons of the interstitial regions and found that there are ~1.5 e per cavity. The ELFs of $Pm\bar{3}m$ MgAl₃, PmmbMgAl and P63/mmc Mg₃Al have also been investigated, as shown in the Fig. S3, (ESI[†]) which exhibit similar interstitial electrons under certain conditions. In this sense, these compounds are considered electrides under high pressure.



Fig. 3 Phonon dispersion curves of the predicted stable Al-Mg structures under high pressure. (a) $Pm\bar{3}m$ MgAl₃ at 90 GPa. (b) P63/mmc MgAl₃ at 100 GPa. (c) P4/mmm MgAl at 40 GPa. (d) Pmmb MgAl at 100 GPa. (e) P63/mmc Mg₃Al at 60 GPa. (f) Fm3m Mg₃Al at 100 GPa. The absence of imaginary frequencies in these structures indicates that they are dynamically stable.

Table 1 The elastic constants C_{ii} (GPa), moduli (bulk modulus B, Young's modulus E and shear modulus G, unit: GPa) and Poisson's ratio ν of the predicted stable Mg-Al compounds under certain pressures. Note that the elastic constants of these structures all meet the mechanical stability criteria, indicating they are mechanically stable

Phase	Pressure	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C ₃₃	C_{44}	C_{55}	C_{66}	В	Ε	G	ν
$Pm\bar{3}m$ MgAl ₃	90 GPa	314.29	251.99					194.80			272.78	257.98	96.09	0.34
P63/mmc MgAl ₃	100 GPa	451.92	281.50	148.91			595.08	112.22		85.55	295.35	308.96	116.53	0.33
P4/mmm MgAl	40 GPa	271.52	62.32	123.52			224.01	102.73		56.91	153.91	201.61	78.65	0.28
Pmmb MgAl	100 GPa	441.53	132.24	250.57	528.05	139.38	435.11	95.52	121.33	115.52	272.06	315.59	120.76	0.31
P63/mmc Mg ₃ Al	60 GPa	276.00	172.64	94.05			340.21	62.30		51.38	178.93	178.35	66.85	0.33
<i>Fm</i> 3 <i>m</i> Mg ₃ Al	100 GPa	249.77	248.93					154.54			249.16	132.41	46.907	0.41

electrons are susceptible to pressure, the charge transfer of by Bader analysis, as depicted in Fig. 5(c). At low pressures

To further illustrate how these anomalous interstitial P63/mmc MgAl₃ under different pressures was analyzed



Fig. 4 The electronic band structures and projected density of states (PDOS) of the predicted stable phases of the Mg–Al compounds. (a) $Pm\overline{3}m$ MgAl₃ at 90 GPa, (b) P63/mmc MgAl₃ at 100 GPa, (c) P4/mmm MgAl at 40 GPa, (d) Pmmb MgAl at 100 GPa, (e) P63/mmc Mg₃Al at 60 GPa and (f) $Fm\overline{3}m$ Mg₃Al at 100 GPa.

 Table 2
 The bader charge on Mg and Al atoms and interstitial areas (X) of phases in the predicted Mg–Al stoichiometric compounds

Phase	Pressure (GPa)	Mg (e per atom)	Al (e per atom)	X (e per f.u.)
Pm3m MgAl ₃	90 GPa	6.52	1.91	4.74
P63/mmc MgAl ₃	100 GPa	6.52	1.79	10.24
P4/mmm MgAl	40 GPa	6.56	4.44	0.00
Pmmb MgAl	100 GPa	6.56	3.21	2.47
P63/mmc Mg ₃ Al	60 GPa	6.62	6.87	0.53
$Fm\bar{3}m$ Mg ₃ Al	100 GPa	7.11	6.63	0.00

(P < 60 GPa), the Bader charges of Mg and Al are almost constant within the pressure range, at about 6.5 e and 3.5 e, respectively. These results reveal the presence of ionic bonds between Mg and Al due to Mg atoms donating their electrons to Al atoms. Similarly, the ionic bonds between Mg and Al can be found in other stable Mg–Al compounds. When the pressure is above 60 GPa, the Bader charge of Al decreases sharply, as opposed to that of Mg, which remains essentially steady under different pressures. It is indicated that excess electrons pile into the interstitial site above 60 GPa, promoting the formation of electrides. These interstitial charges are provided mainly by Al atoms, evidenced by the fact that the integrated charges of Mg atoms remain unchanged. More specifically, at low pressures, there is a small amount of charge transferred from Mg to Al (~ 1.5 e per Mg atom to three Al atoms). Therefore, on increasing the pressure to above 60 GPa, the 3p electrons of Al atoms start to be trapped in the interstitial voids, forming NNAs. In other words, Al atoms gradually reach an ionic state, and the valence electrons gradually reside in the interstitial sites with increasing pressure to form electrides.

For a better understanding of the origin of electride formation, we studied the nearest distance of Al–Al atoms of *P*63/ *mmc* MgAl₃ under different pressures, as shown in the Fig. S4 (ESI†). As a measure of the incompressible core region, an ionic radius of 0.39 Å⁵³ was used for Al, whereas the size of the valence electron cloud is represented by the 3p orbital radius of 1.31 Å.⁵⁴ We found that the nearest distance of Al–Al atoms is 2.62 Å when the 3p orbitals overlap, which corresponds to the electride formation pressure (60 GPa). In this case, the huge Coulomb repulsion compels 3p electrons out of the restraints of the core and into the interstitial sites. Our results thus reveal



Fig. 5 For the *P63/mmc* phase of MgAl₃: (a) Calculated electron localization function (ELF) with an isosurface of 0.75 under 100 GPa. The localized electrons in the interstitial regions are marked in yellow. (b) Charge density under 100 GPa on the (0 0 1) plane. The positions of Mg and Al atoms and the localized electrons in the interstitial regions are marked as "Mg", "Al", and "Inter", respectively. (c) Bader charges of each entity of *P63/mmc* MgAl₃ as a function of pressure. (d) Projected density of states (PDOS) at 100 GPa. X in the PDOS denotes the contributions attributed to the virtual orbitals of the interstitial area.

that, for the given atomic packing environment, only if the nearest Al–Al distance is shorter than the sum of the valence orbitals (2.62 Å) do the electrons begin to be trapped in the interstitial spaces.

The electronic bands of *P*63/*mmc* MgAl₃ show that this phase still exhibits a metallic feature under 100 GPa. To identify the contributions from the NNAs and avoid them being projected onto the 3p orbitals of the neighboring Al atoms, the NNA can be seen as a pseudo-atom in the lattice of the *P*63/*mmc* structure under 100 GPa with a Wigner–Seitz of 1.0 Å. The obtained PDOS curves are shown in Fig. 5(d). We note that the pseudo-atoms have a p-electron character. Although the conducting states of *P*63/*mmc* MgAl₃ derive mainly from the Al-3p states around the Fermi level, they have an important contribution associated with the interstitial electrons.

4. Conclusions

In summary, the different stoichiometries of Mg–Al compounds under pressures of up to 100 GPa have been systematically explored. We identified three novel stable compounds (MgAl₃, MgAl and Mg₃Al) under certain pressures that have not been reported before. In addition, these newly predicted compounds are considered as electrides. The formation of electrides is attributed to the overlaps of the 3p orbitals of the two nearest-neighbor Al atoms that compel the p electrons of Al to be localized in the interstitial cavities. Our current findings will shed light on new electrides of light elements in general and help understand their electronic structures under high pressure.

Conflicts of interest

The authors declare no competing financial interest.

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The numerical calculations in this work were performed in the Hefei advanced computing center and at the Tianhe II supercomputer in Guangzhou.

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