

Predicted Stable Electrides in Mg-Al System under High Pressure

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Computational Details

Pseudopotentials test

In order to test the reliability of the adopted pseudopotentials for Mg and Al, the equation of state (P - V curve) calculated by different exchange-correlation functions, including PBE¹, LDA² and PW91³, was used to compare with the results obtained from the full-potential linearized augmented plane-wave method (LAPW) as implemented in WIEN2K code⁴. As shown in Fig. S1 exemplified by Mg₃Al, the volumes as a function of pressures for Pm-3m structure using PBE potential in VASP⁵ calculations and full-potential WIEN2K calculations are almost identical. The relative enthalpies differences of two phases of Mg₃Al under different pressures (Fig. S1(b)) calculated by these three exchange-correlation functions show a great consistency. Thus, our adopted pseudopotential (GGA_PBE) are valid in the pressure range of 0-100 GPa.

Structure prediction

To search for thermodynamically stable candidates of Mg-Al alloys under pressure, structural predictions were performed via global minimization of free energy surfaces with *ab initio* total-energy calculations as implemented in the swam-

intelligence-based CALYPSO code^{6,7}. The structures of stoichiometry Mg_xAl , ($x= 1/5, 1/4, 1/3, 2/5, 1/2, 3/5, 2/3, 3/4, \& 4/5$) were searched with simulation cell sizes of 1-4 formula units (f.u.) at 20, 40, 60 and 100 GPa, respectively. Random initial structures with certain symmetries were constructed, in which the atomic coordinates were generated following crystallographic symmetry operations. Local optimizations using the VASP code were performed employing the conjugate gradient method and were stopped when energy changes became less than 1×10^{-5} eV per cell. Having obtained the first-generation structures, 60% of them with low Gibbs free energies were selected to serve as next-generation structures by PSO (Particle Swarm Optimization), while the other 40% of the structures in the new generation were randomly generated. As a rule of thumb, structure searches were stopped after 50 generations, which encompass approximately 1000-1200 structures. To further assess the energetics of the structures with accuracy, structures with lower enthalpies were subject to high-precision structural optimization.

Electronic structure analysis

The chemical bonds were analyzed by using electron localization function (ELF)⁸ as done in VASP. The ELF is a well-known indicator of strongly localized electrons and has been proven to be highly valuable in interpreting a broad range of bonding patterns. The calculations of the electronic charge transfer were based on the Bader charge analysis^{9,10} which is an intuitive way of studying charge distribution the charge. Bader¹⁰ defines the atomic charges as integrals over these Bader volumes. Each Bader

volume contains a single electron density maximum and is separated from other volumes by a zero-flux surface of the gradients of the electron density.

Mechanical stability

The elastic constants were calculated using linear response theory¹¹ as implemented by VASP code, and the elastic moduli were calculated based on the Voigt-Reuss-Hill approximations¹². The formulas of mechanical stability criteria¹³ of Mg-Al alloys are listed below.

Tetragonal structure (C_{11} , C_{33} , C_{44} , C_{66} , C_{12} and C_{13}):

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, (C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0$$

Hexagonal structure (C_{11} , C_{33} , C_{44} , C_{12} and C_{13}):

$$C_{44} > 0, C_{11} > |C_{12}|, (C_{11} + 2C_{12})C_{33} > 2C_{13}^2$$

Orthorhombic structure (C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} and C_{23}):

$$C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0, [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, (C_{11} + C_{22} - 2C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, (C_{22} + C_{33} - 2C_{23}) > 0$$

Cubic structure (C_{11} , C_{44} and C_{12}):

$$C_{11} > 0, C_{44} > 0, C_{11} > |C_{12}|, (C_{11} + 2C_{12}) > 0$$

Supplementary Figures

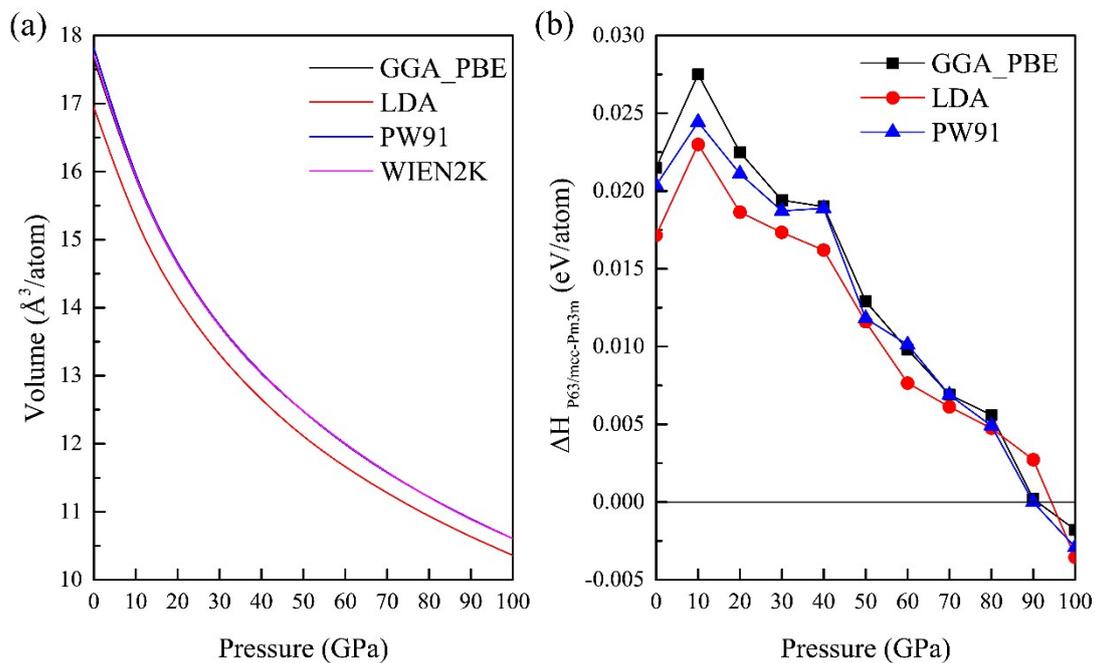


Fig. S1 (a) Volumes as a function of pressures for $\text{Pm-3m Mg}_3\text{Al}$ calculated by using PBE, LDA and PW91 potentials in VASP calculations and full-potential WIEN2K calculations. It is seen that PBE potential and full-potential calculations gave identical results. (b) The enthalpy differences between P63/mmc and $\text{Pm-3m Mg}_3\text{Al}$ as a function of pressures calculated by different exchange-correlation functions, which show a consistence. So, the DFT with GGA_PBE potential calculations are considered to be valid.

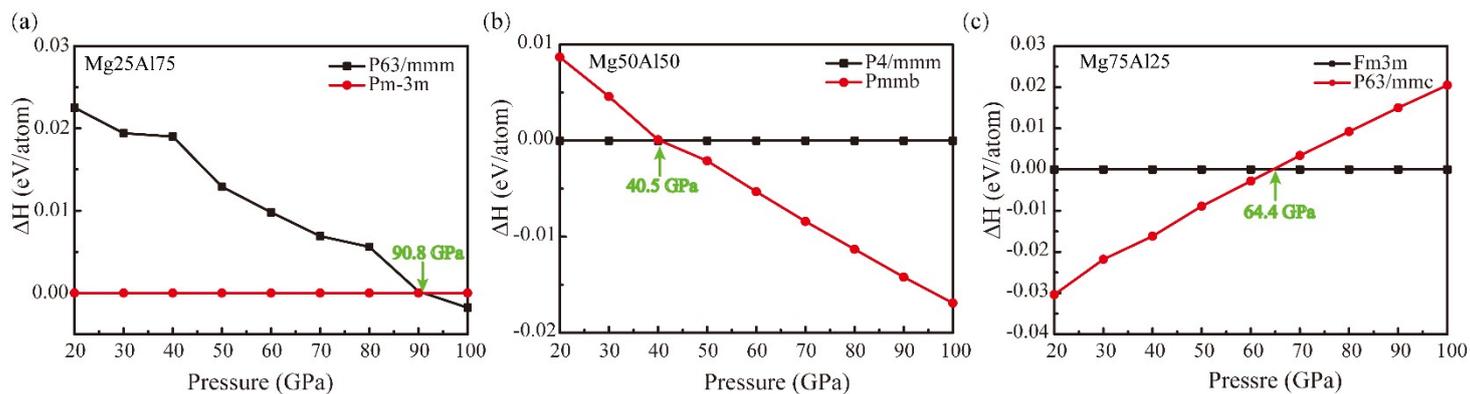


Fig. S2 Enthalpies difference of predicted stable phases of Mg-Al compounds. (a) MgAl₃, (b) MgAl and (c) Mg₃Al.

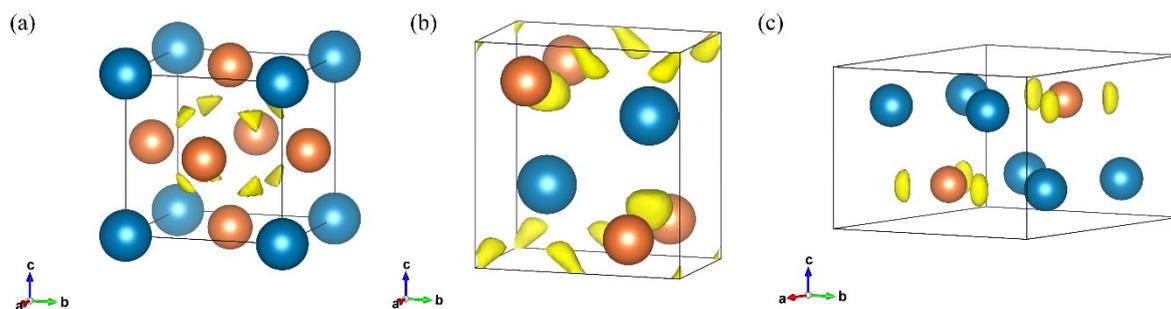


Fig. S3 Electron localization functions (ELF) of structures of Mg-Al compounds with isosurface of 0.75. (a) Pm-3m MgAl₃ under 90 GPa. (b) Pmmb MgAl under 100 GPa and (c) P63/mmc Mg₃Al under 60 GPa. Localized electrons in the interstitials are shown by yellow colors, indicating the formation of electrides. In all these structures, blue and orange spheres represent Mg and Al atoms, respectively.

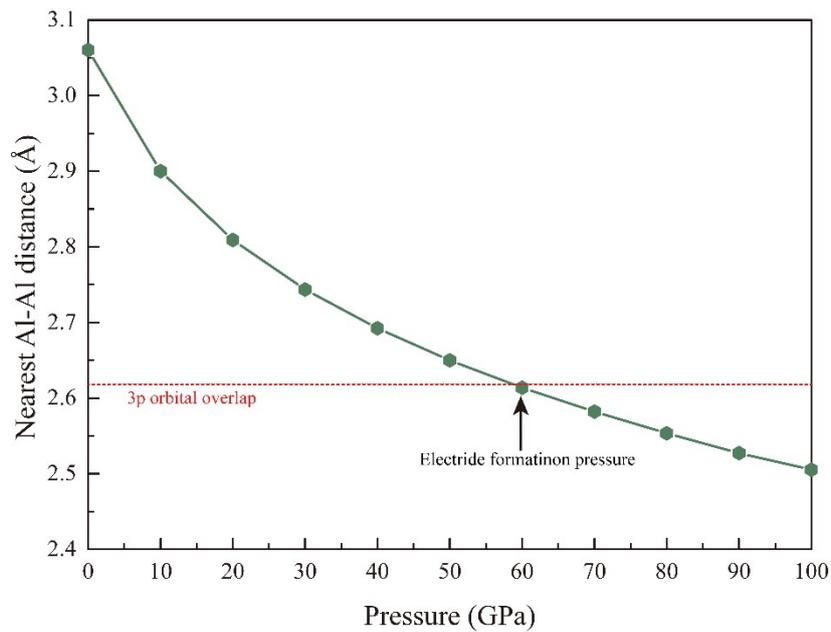


Fig. S4 The nearest Al-Al distance of P63/mmc MgAl₃ under different pressures. Note that, when the 3p orbitals of Al overlap, the nearest Al-Al distance is 2.62 Å, which is corresponding to the electride formation pressure 60 GPa.

Table S1. Structural information of the predicted stable Mg-Al phases.

Phase	Pressure (GPa)	Lattice Parameters (Å, °)	Atoms	Wyckoff Positions (fractional)		
				<i>x</i>	<i>y</i>	<i>z</i>
Pm-3m MgAl ₃	20 GPa	$a = b = c = 3.8782$ $\alpha = \beta = \gamma = 90.0000$	Mg (1a)	0.0000	0.0000	0.0000
			Al (3c)	0.0000	0.5000	0.5000
P63/mmc MgAl ₃	100 GPa	$a = b = 4.9284$ $c = 4.0112$ $\alpha = \beta = 90.0000$ $\gamma = 120$	Mg (2d)	0.3333	0.6667	0.7500
			Al (6h)	0.1657	0.3315	0.2500
P4/mmc MgAl	20 GPa	$a = b = 2.7713$ $c = 4.0080$ $\alpha = \beta = \gamma = 90.0000$	Mg (1b)	0.0000	0.0000	0.5000
			Al (1c)	0.5000	0.5000	0.0000
Pmmb MgAl	100 GPa	$a = 4.0369$ $b = 2.4790$ $c = 4.3199$ $\alpha = \beta = \gamma = 90.0000$	Mg (2f)	0.2500	0.5000	0.3360
			Al (2e)	0.2500	0.0000	0.8382
P63/mmc Mg ₃ Al	50 GPa	$a = 5.3373$ $b = 9.2442$ $c = 4.3196$ $\alpha = \beta = \gamma = 90.0000$	Mg (4c)	0.0000	0.8321	0.2500
			Mg (8g)	0.2518	0.0839	0.2500
			Al (4c)	0.0000	0.3333	0.2500
Fm-3m Mg ₃ Al	100 GPa	$a = b = c = 5.6032$ $\alpha = \beta = \gamma = 90.0000$	Mg (8c)	0.2500	0.2500	0.2500
			Mg (4b)	0.5000	0.5000	0.5000
			Al (4a)	0.0000	0.0000	0.0000

References

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3685.
2. J. P. Perdew and A. Zunger, *Phys. Rev. B* 1981, **23**, 5048.
3. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B* 1992, **46**, 6671.
4. P. Blaha, K. Schwarz, P. Sorantin and S. B. Trickey, *Comput. Phys. Commun.* 1990, **59**, 399.
5. G. Kresse and J. Furthmüller, *Phys. Rev. B* 1996, **54**, 11169.
6. Y. Wang, J. Lv, L. Zhu and Y. Ma, *Phys. Rev. B* **2010**, 82, 094116.
7. Y. Wang, J. Lv, L. Zhu and Y. Ma, *Comput. Phys. Commun.* 2012, **183**, 2063.
8. A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* 1990, **92**, 5397.
9. R. F. Bader, *Acc. Che. Res.* 1985, **18**, 9.
10. G. Henkelman, A. Arnaldsson and H. Jónsson, *Comput. Mater. Sci.* 2006, **36**, 354.
11. S. Baroni, P. Giannozzi and A. Testa, *Phys. Rev. Lett.* 1987, **59**, 2662.
12. R. Hill, *Proc. Phys. Soc. Sect. A* 1952, **65**, 349.
13. J. F. Pugh, Oxford university press, Oxford, 1985