Electronic Supplementary Material (ESI) for RSC Advances

Why host to dopant energy transfer is absent in $MgAl_2O_4:Eu^{3+}$ spinel? And exploring Eu^{3+} site distribution and local symmetry through its photoluminescence: interplay of experiment and theory

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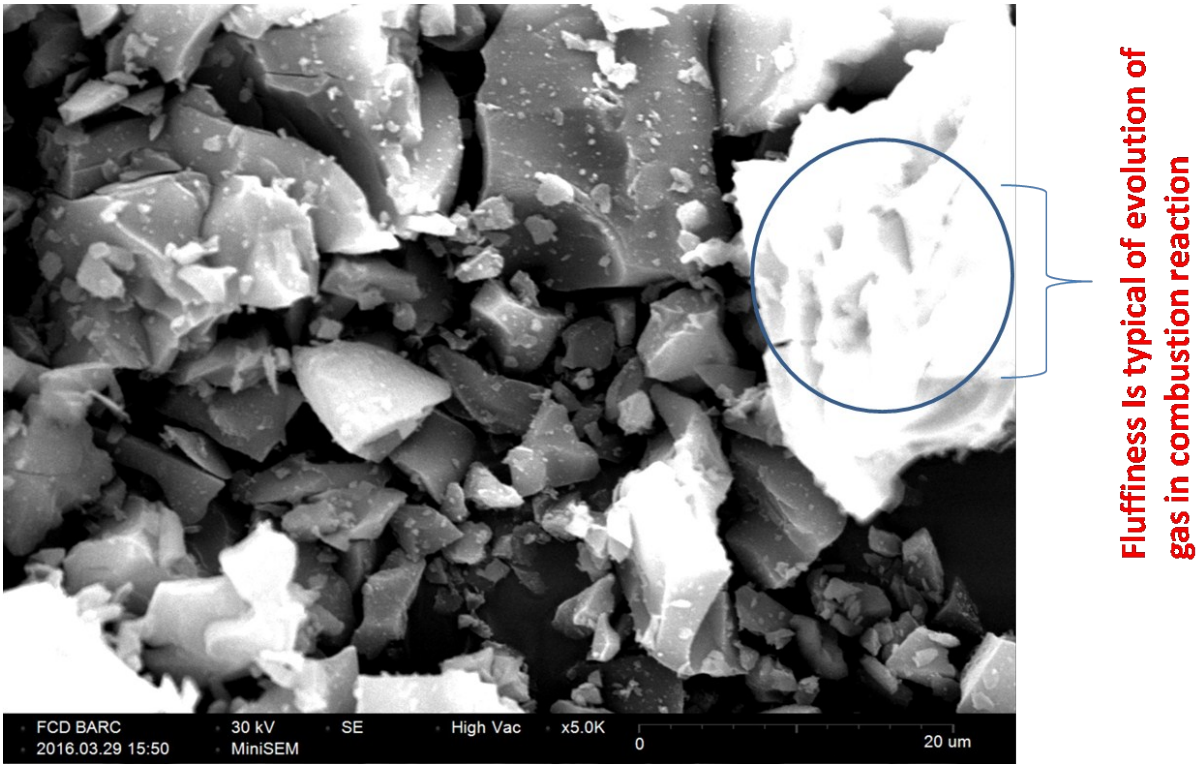

Figure S1: Scanning electron micrograph of $MgAl_2O_4:Eu^{3+}$

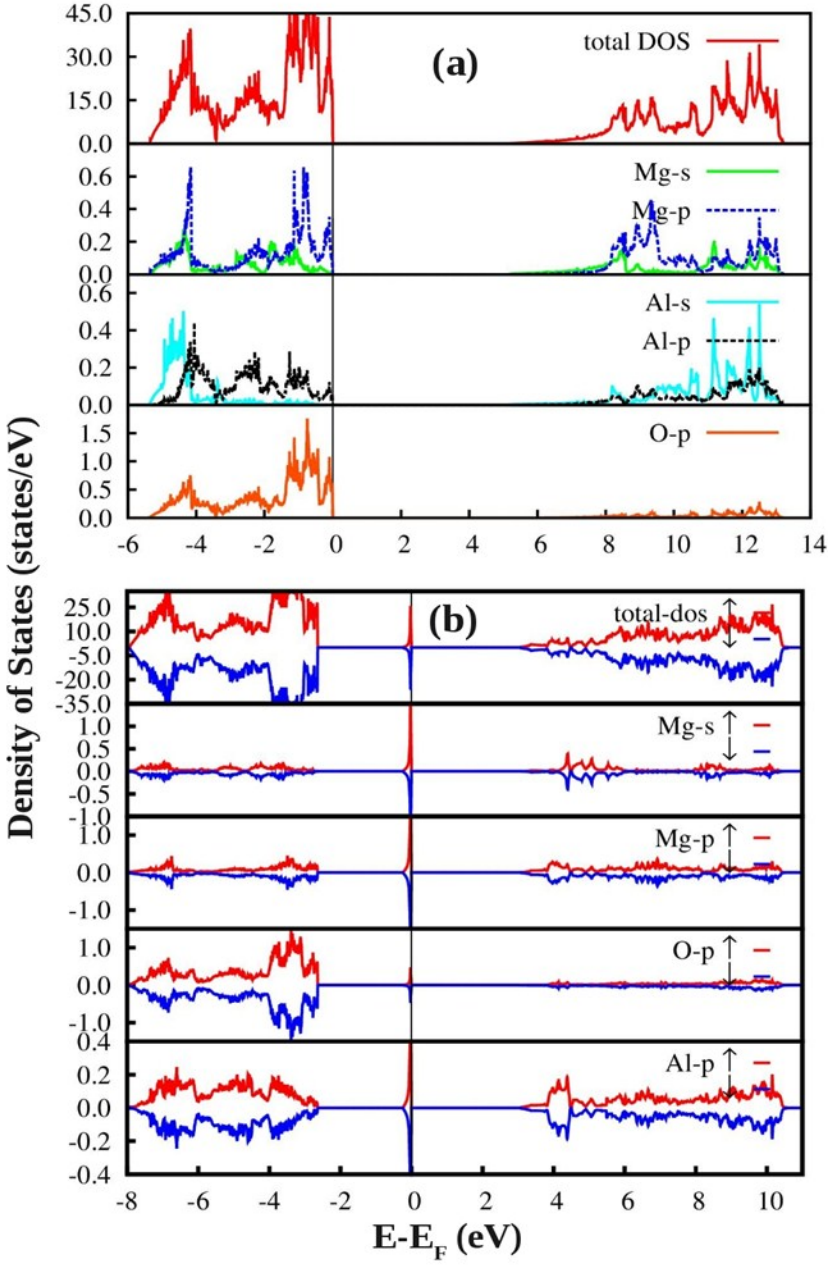

Figure S2: Total and angular momentum decomposed density of states (DOS) of normal spinel pure $MgAl_2O_4$ (a) and neutral oxygen vacancy in $MgAl_2O_4$ (b). Vertical lines at zero energy represent Fermi energy.

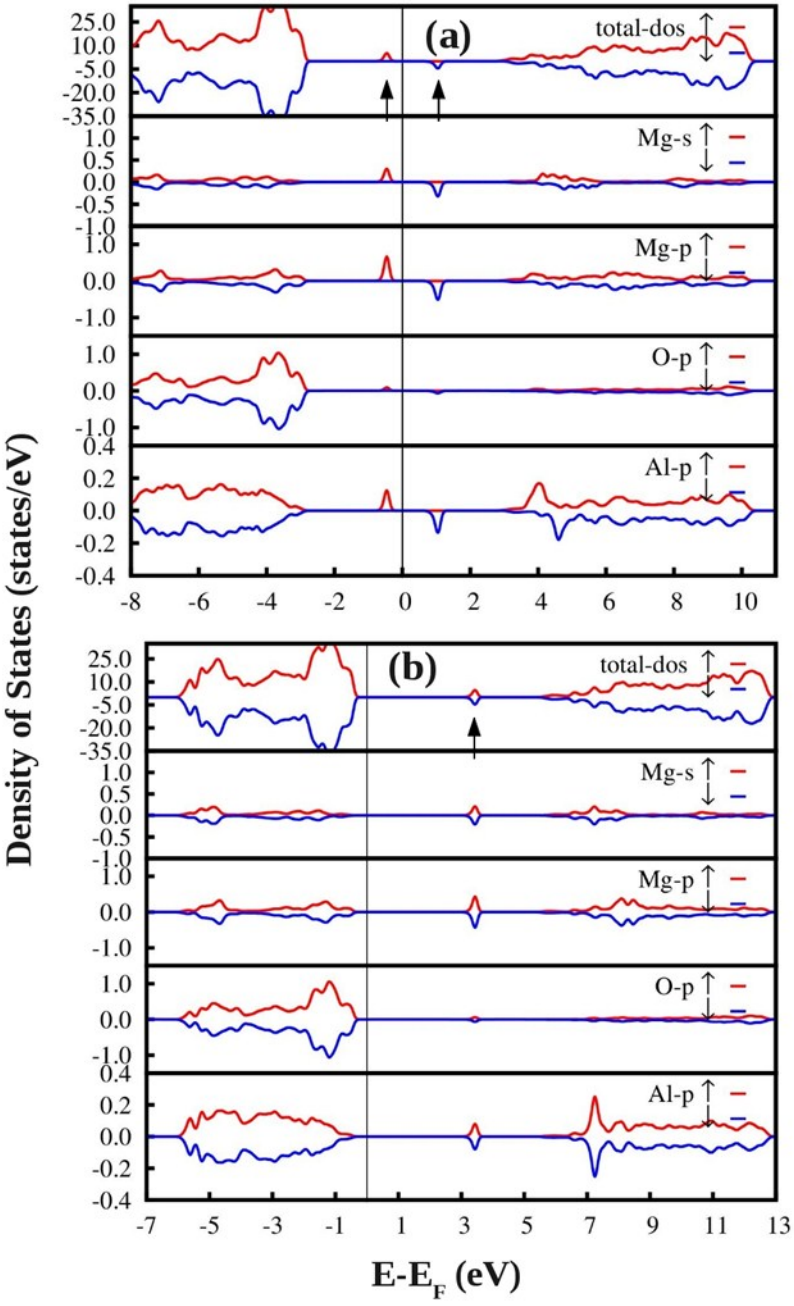

Figure S3: Total and angular momentum decomposed density of states (DOS) of normal spinel $MgAl_2O_4$ with +1 charged O defect (V_O^{+1}) (a) and +2 charged O defect (V_O^{+2}) (b). Vertical lines at zero energy represent Fermi energy. Impurity states are marked by arrows in this figure.

GGA-PBE optimized atomic positions of normal $MgAl_2O_4$ unitcell in direct lattice coordinates

Unit-cell vectors

8.1599835824156717 0.0000000000000000 0.0000000000000000

0.0000000000000000 8.1599835824156717 0.0000000000000000

0.0000000000000000 0.0000000000000000 8.1599835824156717

Atomic Positions

 # Mg atoms

0.1250000000000000 0.1250000000000000 0.1250000000000000

0.8750000000000000 0.8750000000000000 0.8750000000000000

0.6250000000000000 0.1250000000000000 0.6250000000000000

0.3750000000000000 0.8750000000000000 0.3750000000000000

0.1250000000000000 0.6250000000000000 0.6250000000000000

0.8750000000000000 0.3750000000000000 0.3750000000000000

0.6250000000000000 0.6250000000000000 0.1250000000000000

0.3750000000000000 0.3750000000000000 0.8750000000000000

 # Al atoms

0.5000000000000000 0.5000000000000000 0.5000000000000000

0.2500000000000000 0.7500000000000000 0.0000000000000000

0.7500000000000000 0.2500000000000000 0.0000000000000000

0.7500000000000000 0.0000000000000000 0.2500000000000000

0.2500000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 0.2500000000000000 0.7500000000000000

0.0000000000000000 0.7500000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.0000000000000000

0.2500000000000000 0.2500000000000000 0.5000000000000000

0.7500000000000000 0.7500000000000000 0.5000000000000000

0.7500000000000000 0.5000000000000000 0.7500000000000000

0.2500000000000000 0.5000000000000000 0.2500000000000000

0.0000000000000000 0.5000000000000000 0.0000000000000000

0.5000000000000000 0.2500000000000000 0.2500000000000000

0.5000000000000000 0.7500000000000000 0.7500000000000000

0.0000000000000000 0.0000000000000000 0.5000000000000000

 # O atoms

0.2634140211611803 0.2634140211611803 0.2634140211611803

0.7365859788388198 0.7365859788388198 0.7365859788388198

0.4865859788388197 -0.0134140211611803 0.7634140211611802

0.5134140211611802 0.0134140211611803 0.2365859788388197

-0.0134140211611803 0.7634140211611802 0.4865859788388197

0.0134140211611803 0.2365859788388197 0.5134140211611802

0.7634140211611802 0.4865859788388197 -0.0134140211611803

0.2365859788388197 0.5134140211611802 0.0134140211611803

0.0134140211611803 0.5134140211611802 0.2365859788388197

-0.0134140211611803 0.4865859788388197 0.7634140211611802

0.5134140211611802 0.2365859788388197 0.0134140211611803

0.4865859788388197 0.7634140211611802 -0.0134140211611803

0.2365859788388197 0.0134140211611803 0.5134140211611802

0.7634140211611802 -0.0134140211611803 0.4865859788388197

0.2634140211611803 0.7634140211611802 0.7634140211611802

0.7365859788388198 0.2365859788388197 0.2365859788388197

0.4865859788388197 0.4865859788388197 0.2634140211611803

0.5134140211611802 0.5134140211611802 0.7365859788388198

-0.0134140211611803 0.2634140211611803 -0.0134140211611803

0.0134140211611803 0.7365859788388198 0.0134140211611803

0.0134140211611803 0.0134140211611803 0.7365859788388198

-0.0134140211611803 -0.0134140211611803 0.2634140211611803

0.5134140211611802 0.7365859788388198 0.5134140211611802

0.4865859788388197 0.2634140211611803 0.4865859788388197

0.7634140211611802 0.2634140211611803 0.7634140211611802

0.2365859788388197 0.7365859788388198 0.2365859788388197

0.2634140211611803 0.4865859788388197 0.4865859788388197

0.7365859788388198 0.5134140211611802 0.5134140211611802

0.7365859788388198 0.0134140211611803 0.0134140211611803

0.2634140211611803 -0.0134140211611803 -0.0134140211611803

0.7634140211611802 0.7634140211611802 0.2634140211611803

0.2365859788388197 0.2365859788388197 0.7365859788388198

GGA-PBE optimized atomic positions of normal $MgAl_2O_4$ unitcell with Eu atom doped in Al site in direct lattice coordinates

Unit-cell Vectors

8.2469060614457455 0.0349587867376875 0.0349587867376875

0.0349587867376875 8.2469060614457455 0.0349587867376875

0.0349587867376875 0.0349587867376875 8.2469060614457455

 # Mg atoms

0.1205179740997768 0.1205179740997768 0.1205179740997768

0.8794820259002232 0.8794820259002232 0.8794820259002232

0.6262393453310173 0.1189219869405830 0.6262393453310173

0.3737606546689830 0.8810780130594168 0.3737606546689830

0.1189219869405830 0.6262393453310173 0.6262393453310173

0.8810780130594168 0.3737606546689830 0.3737606546689830

0.6262393453310173 0.6262393453310173 0.1189219869405830

0.3737606546689830 0.3737606546689830 0.8810780130594168

 # Al atoms

0.2498038690644292 0.7501961309355708 -0.0000000000000000

0.7501961309355708 0.2498038690644292 0.0000000000000000

0.7501961309355708 0.0000000000000000 0.2498038690644292

0.2498038690644292 -0.0000000000000000 0.7501961309355708

0.0000000000000000 0.2498038690644292 0.7501961309355708

-0.0000000000000000 0.7501961309355708 0.2498038690644292

0.5000000000000000 -0.0000000000000000 0.0000000000000000

0.2406039647137115 0.2406039647137115 0.4935702863123445

0.7593960352862886 0.7593960352862886 0.5064297136876555

0.7593960352862886 0.5064297136876555 0.7593960352862886

0.2406039647137116 0.4935702863123445 0.2406039647137115

-0.0000000000000000 0.5000000000000000 0.0000000000000000

0.4935702863123445 0.2406039647137115 0.2406039647137116

0.5064297136876555 0.7593960352862886 0.7593960352862886

0.0000000000000000 -0.0000000000000000 0.5000000000000000

 # O atoms

0.2568836943145249 0.2568836943145250 0.2568836943145249

0.7431163056854753 0.7431163056854753 0.7431163056854753

0.4860001091616526 0.9902575008067422 0.7692325573777578

0.5139998908383474 0.0097424991932578 0.2307674426222426

0.9902575008067422 0.7692325573777578 0.4860001091616526

0.0097424991932578 0.2307674426222425 0.5139998908383474

0.7692325573777578 0.4860001091616526 0.9902575008067422

0.2307674426222425 0.5139998908383474 0.0097424991932578

0.0097424991932578 0.5139998908383474 0.2307674426222425

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0.5139998908383474 0.2307674426222425 0.0097424991932578

0.4860001091616526 0.7692325573777578 0.9902575008067422

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0.7692325573777578 0.9902575008067422 0.4860001091616526

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0.4752803481294807 0.4752803481294807 0.2305240084782191

0.5247196518705194 0.5247196518705194 0.7694759915217808

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0.0150643888968678 0.0150643888968678 0.7385714357711110

0.9849356111031324 0.9849356111031324 0.2614285642288886

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0.2305240084782191 0.4752803481294807 0.4752803481294807

0.7694759915217808 0.5247196518705194 0.5247196518705194

0.7385714357711110 0.0150643888968678 0.0150643888968678

0.2614285642288886 0.9849356111031324 0.9849356111031324

0.7624915425829440 0.7624915425829440 0.2667768891172829

0.2375084574170559 0.2375084574170559 0.7332231108827169

 # Eu atom

0.5000000000000000 0.5000000000000000 0.5000000000000000

GGA-PBE optimized atomic positions of normal $MgAl_2O_4$ unitcell with Eu atom doped in Mg site in direct lattice coordinates

Unit-cell Vectors

8.2522065492237573 0.0000000000000000 -0.0000000000000000

0.0000000000000000 8.2522065492237573 -0.0000000000000000

0.0000000000000000 0.0000000000000000 8.2522065492237573

 # Mg atoms

0.8725956968003652 0.8725956968003652 0.8725956968003652

0.6250000000000000 0.1250000000000000 0.6250000000000000

0.3774043031996347 0.8725956968003652 0.3774043031996347

0.1250000000000000 0.6250000000000000 0.6250000000000000

0.8725956968003652 0.3774043031996347 0.3774043031996347

0.6250000000000000 0.6250000000000000 0.1250000000000000

0.3774043031996347 0.3774043031996347 0.8725956968003652

 # Al atoms

0.5013823520847743 0.5013823520847743 0.5013823520847743

0.2536871214031990 0.7432549711611507 -0.0036871214031990

0.7432549711611507 0.2536871214031990 -0.0036871214031990

0.7432549711611507 -0.0036871214031990 0.2536871214031990

0.2536871214031990 -0.0036871214031990 0.7432549711611507

-0.0036871214031990 0.2536871214031990 0.7432549711611507

-0.0036871214031990 0.7432549711611507 0.2536871214031990

0.5067450288388493 -0.0036871214031990 -0.0036871214031990

0.2536871214031990 0.2536871214031990 0.5067450288388493

0.7486176479152257 0.7486176479152257 0.5013823520847743

0.7486176479152257 0.5013823520847743 0.7486176479152257

0.2536871214031990 0.5067450288388493 0.2536871214031990

-0.0036871214031990 0.5067450288388493 -0.0036871214031990

0.5067450288388493 0.2536871214031990 0.2536871214031990

0.5013823520847743 0.7486176479152257 0.7486176479152257

-0.0036871214031990 -0.0036871214031990 0.5067450288388493

 # O atoms

0.2742260957837422 0.2742260957837423 0.2742260957837423

0.7356367069679166 0.7356367069679166 0.7356367069679166

0.4890172616724697 0.9843924557573770 0.7609827383275304

0.5111825746762668 0.0145585359640714 0.2354414640359286

0.9843924557573770 0.7609827383275304 0.4890172616724697

0.0145585359640714 0.2354414640359286 0.5111825746762668

0.7609827383275304 0.4890172616724697 0.9843924557573770

0.2354414640359286 0.5111825746762668 0.0145585359640714

0.0145585359640714 0.5111825746762668 0.2354414640359286

0.9843924557573770 0.4890172616724697 0.7609827383275304

0.5111825746762668 0.2354414640359286 0.0145585359640714

0.4890172616724697 0.7609827383275304 0.9843924557573770

0.2354414640359286 0.0145585359640714 0.5111825746762668

0.7609827383275304 0.9843924557573770 0.4890172616724697

0.2656075442426230 0.7609827383275304 0.7609827383275304

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0.4890172616724697 0.4890172616724697 0.2656075442426230

0.5143632930320834 0.5143632930320834 0.7356367069679166

0.9757739042162580 0.2742260957837423 0.9757739042162580

0.0145585359640714 0.7388174253237332 0.0145585359640714

0.0145585359640714 0.0145585359640714 0.7388174253237332

0.9757739042162580 0.9757739042162580 0.2742260957837423

0.5143632930320834 0.7356367069679166 0.5143632930320834

0.4890172616724697 0.2656075442426230 0.4890172616724697

0.7609827383275304 0.2656075442426230 0.7609827383275304

0.2354414640359286 0.7388174253237332 0.2354414640359286

0.2656075442426230 0.4890172616724697 0.4890172616724697

0.7356367069679166 0.5143632930320834 0.5143632930320834

0.7388174253237332 0.0145585359640714 0.0145585359640714

0.2742260957837423 0.9757739042162580 0.9757739042162580

0.7609827383275304 0.7609827383275304 0.2656075442426230

0.2354414640359286 0.2354414640359286 0.7388174253237332

 # Eu atom

0.1250000000000000 0.1250000000000000 0.1250000000000000

GGA-PBE optimized atomic positions of normal $MgAl_2O_4$ unitcell with neutral vacancy (V_0^O) in direct lattice coordinates

Unit-cell Vectors

8.1552094451108132 -0.0078267026088766 0.0078267026088766

-0.0078267026088766 8.1552094451108132 0.0078267026088766

0.0078267026088766 0.0078267026088766 8.1552094451108132

 # Mg atoms

0.1257524257994415 0.1257524257994415 0.1242475742005585

0.8745154857333600 0.8745154857333600 0.8754499159889590

0.6247363001454044 0.1258117040937318 0.6252636998545956

0.3745500840110411 0.8745154857333600 0.3754845142666399

0.1258117040937318 0.6247363001454044 0.6252636998545956

0.8745154857333600 0.3745500840110411 0.3754845142666399

0.6247363001454044 0.6247363001454044 0.1241882959062682

0.3879985721024983 0.3879985721024983 0.8620014278975018

 # Al atoms

0.4986519919229579 0.4986519919229579 0.5004486123653521

0.2496431229107733 0.7499647935769136 0.0003568770892267

0.7499647935769136 0.2496431229107733 0.0003568770892267

0.7495334588455566 0.9997547187824796 0.2502452812175204

0.2503611140984408 0.0015824052739569 0.7507312248266615

0.0015824052739569 0.2503611140984408 0.7507312248266615

0.9997547187824796 0.7495334588455566 0.2502452812175204

0.4992687751733382 0.0015824052739569 0.9996388859015591

0.2496431229107733 0.2496431229107733 0.5000352064230865

0.7494224399669387 0.7494224399669387 0.5005775600330613

0.7495513876346479 0.4986519919229579 0.7513480080770424

0.2503611140984408 0.4992687751733382 0.2484175947260431

0.0015824052739569 0.4992687751733382 0.9996388859015592

0.4992687751733382 0.2503611140984408 0.2484175947260431

0.4986519919229579 0.7495513876346479 0.7513480080770424

0.9997547187824796 0.9997547187824796 0.5004665411544434

 # O atoms

0.2632642945022813 0.2632642945022813 0.2636025158342331

0.7342305656392660 0.7342305656392660 0.7377802959594879

0.4867846562782551 0.9860318561032391 0.7632153437217452

0.5127677368032924 0.0135320027782457 0.2364679972217543

0.9856916336265719 0.7625845231495009 0.4874154768504991

0.0131051280658962 0.2362862483808351 0.5138192956056126

0.7640085608072172 0.4860070879338497 0.9875760826762155

0.2382883183539100 0.5130403455468272 0.0117116816460901

0.0135320027782457 0.5127677368032924 0.2364679972217543

0.9860318561032391 0.4867846562782551 0.7632153437217452

0.5130403455468272 0.2382883183539100 0.0117116816460901

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0.2624239173237845 0.7640085608072172 0.7639929120661503

0.7361807043943874 0.2362862483808351 0.2368948719341037

0.4867846562782551 0.4867846562782551 0.2639681438967610

0.9863974841657670 0.2632642945022813 0.9867357054977188

0.0131051280658962 0.7361807043943874 0.0137137516191649

0.0135320027782457 0.0135320027782457 0.7372322631967076

0.9863832772638798 0.9863832772638798 0.2636167227361201

0.5122197040405121 0.7342305656392660 0.5157694343607340

0.4860070879338497 0.2624239173237845 0.4859914391927830

0.7640085608072172 0.2624239173237845 0.7639929120661503

0.2362862483808351 0.7361807043943874 0.2368948719341037

0.2624239173237845 0.4860070879338497 0.4859914391927830

0.7342305656392660 0.5122197040405121 0.5157694343607340

0.7361807043943874 0.0131051280658962 0.0137137516191649

0.2632642945022813 0.9863974841657670 0.9867357054977188

0.7625845231495009 0.7625845231495009 0.2643083663734282

0.2382883183539100 0.2382883183539100 0.7369596544531728

GGA-PBE optimized atomic positions of normal $MgAl_2O_4$ unitcell with +1 charged O vacancy (V_0^{+1}) in direct lattice coordinates

Unit-cell Vectors

8.1201966531138954 -0.0198265586120434 0.0198265586120434

-0.0198265586120434 8.1201966531138954 0.0198265586120434

0.0198265586120434 0.0198265586120434 8.1201966531138954

 # Mg atoms

0.1246249608971346 0.1246249608971346 0.1253750391028654

0.8733922561582625 0.8733922561582625 0.8765053536716604

0.6269904925791702 0.1298170129653332 0.6230095074208298

0.3734946463283397 0.8733922561582625 0.3766077438417375

0.1298170129653332 0.6269904925791702 0.6230095074208298

0.8733922561582625 0.3734946463283397 0.3766077438417375

0.6269904925791702 0.6269904925791702 0.1201829870346668

0.3763087373526623 0.3763087373526623 0.8736912626473374

 # Al atoms

0.4992855656912972 0.4992855656912972 0.4839499359304159

0.2493032517327878 0.7504341031326808 0.0006967482672122

0.7504341031326808 0.2493032517327878 0.0006967482672122

0.7493211821690861 0.9993076935714071 0.2506923064285930

0.2485928060110127 0.0021115400457495 0.7509150566222563

0.0021115400457495 0.2485928060110127 0.7509150566222563

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0.4990849433777438 0.0021115400457495 0.0014071939889873

0.2493032517327878 0.2493032517327878 0.4995658968673192

0.7494821937216400 0.7494821937216400 0.5005178062783601

0.7660500640695843 0.4992855656912972 0.7507144343087023

0.2485928060110127 0.4990849433777438 0.2478884599542505

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0.4992855656912972 0.7660500640695843 0.7507144343087023

0.9993076935714071 0.9993076935714071 0.5006788178309141

 # O atoms

0.2633879076123778 0.2633879076123778 0.2634492209147051

0.7297698460969411 0.7297698460969411 0.7401184795348635

0.4874788317157242 0.9927025742747501 0.7625211682842759

0.5121405301253577 0.0123243551843196 0.2376756448156804

0.9842517180279162 0.7610323274152507 0.4889676725847492

0.0128036132505639 0.2364652853852425 0.5144671678321221

0.7634199762099592 0.4866381909088414 0.9838721272026291

0.2377707437886337 0.5133266426016553 0.0122292562113663

0.0123243551843196 0.5121405301253577 0.2376756448156804

0.9927025742747501 0.4874788317157242 0.7625211682842759

0.5133266426016553 0.2377707437886337 0.0122292562113663

0.4866381909088414 0.7634199762099592 0.9838721272026291

0.2364652853852425 0.0128036132505639 0.5144671678321221

0.7610323274152507 0.9842517180279162 0.4889676725847492

0.2661278727973709 0.7634199762099592 0.7633618090911586

0.7355328321678779 0.2364652853852425 0.2371963867494361

0.4874788317157242 0.4874788317157242 0.2572974257252498

0.9865507790852950 0.2633879076123778 0.9866120923876223

0.0128036132505639 0.7355328321678779 0.0135347146147575

0.0123243551843196 0.0123243551843196 0.7378594698746423

0.9855094182594979 0.9855094182594979 0.2644905817405023

0.5098815204651365 0.7297698460969411 0.5202301539030589

0.4866381909088414 0.2661278727973709 0.4865800237900408

0.7634199762099592 0.2661278727973709 0.7633618090911586

0.2364652853852425 0.7355328321678779 0.2371963867494361

0.2661278727973709 0.4866381909088414 0.4865800237900408

0.7297698460969411 0.5098815204651365 0.5202301539030589

0.7355328321678779 0.0128036132505639 0.0135347146147575

0.2633879076123778 0.9865507790852950 0.9866120923876223

0.7610323274152507 0.7610323274152507 0.2657482819720838

0.2377707437886337 0.2377707437886337 0.7366733573983447

GGA-PBE optimized atomic positions of normal $MgAl_2O_4$ unitcell with +2 charged O vacancy (V_0^{+2}) in direct lattice coordinates

Unit-cell Vectors

8.0917734033390456 -0.0381903003926540 0.0381903003926540

-0.0381903003926540 8.0917734033390456 0.0381903003926540

0.0381903003926540 0.0381903003926540 8.0917734033390456

 # Mg atoms

0.1226069406730265 0.1226069406730265 0.1273930593269735

0.8718729976333086 0.8718729976333086 0.8772186892710766

0.6300243016390107 0.1347460479621842 0.6199756983609893

0.3727813107289233 0.8718729976333086 0.3781270023666915

0.1347460479621842 0.6300243016390107 0.6199756983609893

0.8718729976333086 0.3727813107289233 0.3781270023666915

0.6300243016390107 0.6300243016390107 0.1152539520378159

0.3538301311649478 0.3538301311649477 0.8961698688350526

 # Al atoms

0.5017229530706145 0.5017229530706145 0.4682020927157212

0.2491974454064237 0.7507120660814266 0.0008025545935763

0.7507120660814266 0.2491974454064237 0.0008025545935763

0.7487150015302286 -0.0014212364753718 0.2514212364753720

0.2465582692945978 0.0016031427203382 0.7505301832940757

0.0016031427203382 0.2465582692945978 0.7505301832940757

-0.0014212364753718 0.7487150015302286 0.2514212364753720

0.4994698167059241 0.0016031427203382 0.0034417307054022

0.2491974454064237 0.2491974454064237 0.4992879339185735

0.7494780510084051 0.7494780510084051 0.5005219489915947

0.7817979072842790 0.5017229530706145 0.7482770469293852

0.2465582692945978 0.4994698167059241 0.2483968572796618

0.0016031427203382 0.4994698167059241 0.0034417307054022

0.4994698167059241 0.2465582692945978 0.2483968572796618

0.5017229530706145 0.7817979072842790 0.7482770469293852

-0.0014212364753718 -0.0014212364753718 0.5012849984697714

 # O atoms

0.2632134351238641 0.2632134351238641 0.2626677577743797

0.7257663258279055 0.7257663258279055 0.7420923351872747

0.4880981669604681 0.0022015927936166 0.7619018330395320

0.5119318420306160 0.0111596739120391 0.2388403260879609

0.9827711544131432 0.7594802184126683 0.4905197815873316

0.0127136998716512 0.2366101802647759 0.5147986630891698

0.7637765540461153 0.4874534314588099 0.9795073513152970

0.2367545398036092 0.5150267766842413 0.0132454601963907

0.0111596739120391 0.5119318420306160 0.2388403260879609

0.0022015927936166 0.4880981669604681 0.7619018330395320

0.5150267766842413 0.2367545398036092 0.0132454601963907

0.4874534314588099 0.7637765540461153 0.9795073513152970

0.2366101802647759 0.0127136998716512 0.5147986630891698

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0.2704926486847029 0.7637765540461153 0.7625465685411904

0.7352013369108302 0.2366101802647759 0.2372863001283488

0.4880981669604681 0.4880981669604681 0.2477984072063834

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0.0111596739120391 0.0111596739120391 0.7380681579693840

0.9842022149391829 0.9842022149391829 0.2657977850608170

0.5079076648127253 0.7257663258279055 0.5242336741720945

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0.7257663258279055 0.5079076648127253 0.5242336741720945

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0.2632134351238641 0.9873322422256204 0.9867865648761358

0.7594802184126683 0.7594802184126683 0.2672288455868568

0.2367545398036092 0.2367545398036092 0.7349732233157587