Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Ag_6Cl_4: the first silver chloride with rare Ag_6 clusters from an *ab initio* study

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TABLE OF CONTENT

E1. Computational details

The optimizations and electronic structure calculations were carries out without any symmetry constrains using DFT-GGA PBEsol functional[1] with added on-site electron correction on Ag *d* orbitals using DFT+U approach according to Liechtenstein[2] with U_{Ag}= 5 eV and J_{Ag}= 1 eV, [3] and with added Grimme correction with Becke-Jonson damping (D3)[4] for weaker dispersive interactions (chlorine) as implemented in VASP package.[5] Electronic structure was additionally calculated with hybrid DFT functional HSE06 with 25% of exact exchange[6] improved for the dispersive correction D3.

Lattice dynamics including phonon dispersion curves (Figures E1 and E2), phonon density of states (Figures E3 and E4) and Γ-point frequencies (Tables E1 and E2) was calculated using phonon direct method with supercell approach (80 atoms) in program PHONONY[7] on DFT-D3 and DFT-D3+U level and comparable results were obtained with both methods.

References

1 G.I. Csonka, J.P. Perdew, A. Ruzsinszky, P.H.T. Philipsen, J. Lebégue, O.A. Paier, J. G. Vydrov and Ángyán, *Phys. Rev. B*, 2009, **79**, 155107.

2 A.I. Liechtenstein, V.I. Anisimov, J. Zaanen, *Phys. Rev. B*, 1995, **52**, R5467(R).

3 This set of U,J parameters has reliably reproduced experimental data for variety of systems with partially opened Ag d shell. See for example: (a) D. Kasinathan, K. Koepernik, U. Nitzsche and H Rosner, *Phys Rev Lett*, 2007, **99**, 247210; (b) A. Grzelak, J. Gawraczyński, T. Jaroń, D. Kurzydłowski, Z. Mazej, P. J. Leszczyński, Vitali B. Prakapenka, M. Derzsi, V. V. Struzhkin and W. Grochala, *Dalton Trans.*, 2017, **46**, 14742–14745; (c) P.J. Malinowski, M. Derzsi, Z. Mazej, Z. Jagličić, B. Gaweł, W. Łasocha and W. Grochala, *Angew. Chem. Int. Ed. Engl.*, 2010, **49**(9), 1683–1686.

4 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem.*, 2011, **32**, 1456.

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E2. Phonon dispersion curves

Ag_6Cl_4 was computed to be dynamically stable on both DFT-D3 and DFT-D3+U level: all frequencies are real (gain positive values).

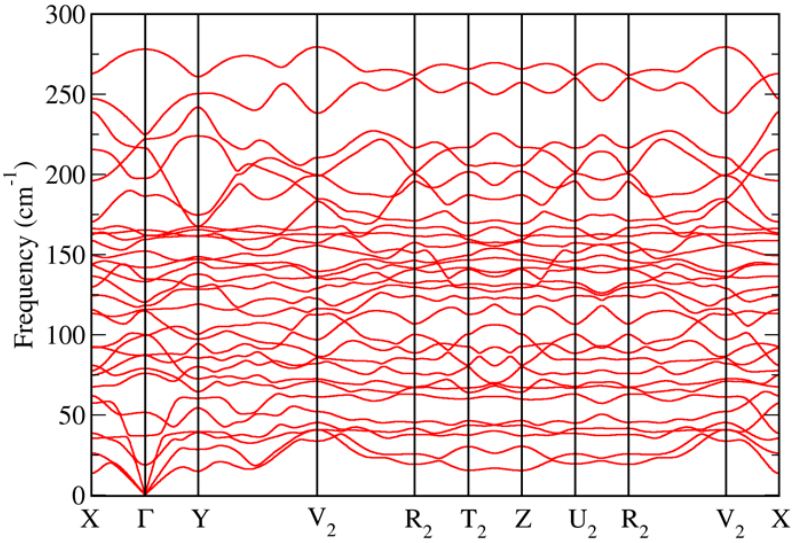

Figure E1. Phonon dispersion curves calculated forAg_6Cl_4 at DFT-D3+U level. The path in Brillouin zone: X (0.5, 0.0, 0.0), Γ(0.0, 0.0, 0.0), Y (0.0, 0.5, 0.0), V_2 (0.5, -0.5, 0), R_2 (-0.5, -0.5, 0.5) , T_2 (0, -0.5, 0.5), Z (0, 0, 0.5), U_2 (-0.5, 0, 0.5).

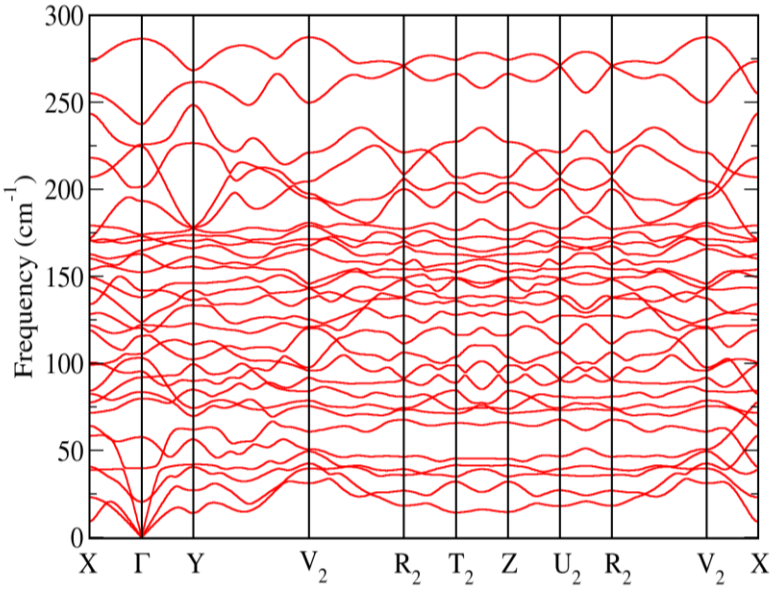

Figure E2. Phonon dispersion curves calculated forAg_6Cl_4 at DFT-D3 level. The path in Brillouin zone: as in Figure E1.

E3. Phonon density of states

The phonon density of states of Ag_6Cl_4 is spread within the range 0–280 cm^{-1} with considerable contribution from Cl atoms in the entire region. The Ag vibrations dominate below 100 cm^{-1} and strongly couple with Cl in the intermediate range of 100–180cm^{-1}. Comparable result is obtained on DFT-D3 and DFT-D3+U level.

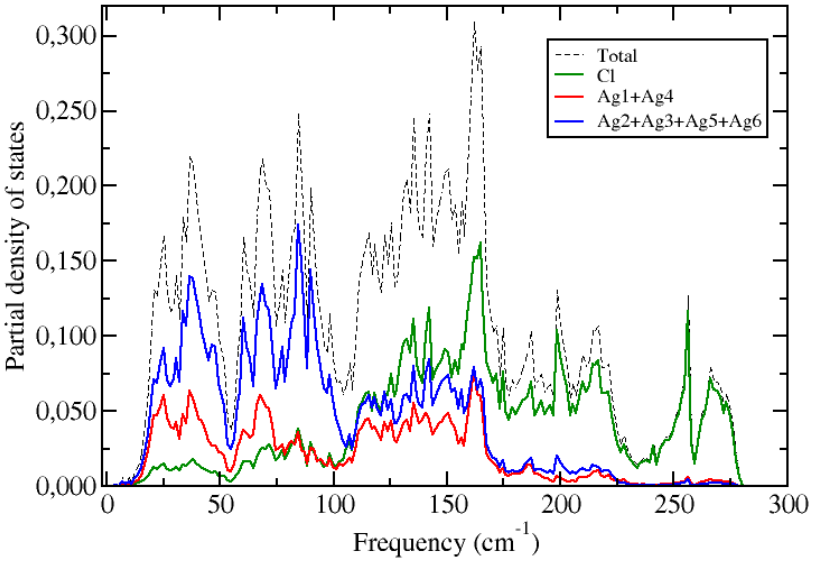

Figure E3. Atom-projected phonon density of states of Ag_6Cl_4 calculated at DFT-D3+U level.

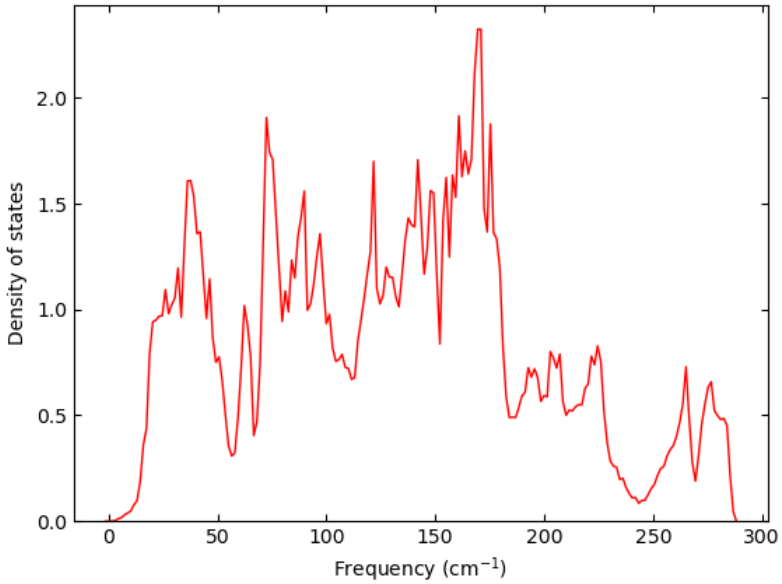

Figure E4. Phonon density of states of Ag_6Cl_4 calculated at DFT-D3 level.

E3. Γ-point modes

Table E1. List of Γ-point frequencies calculated for Ag_6Cl_4 at DFT-D3+U level. Irrep – irreducible representation, IR – infrared active, R – Raman active.

Mode no.	Irrep	Optical activity	E (cm^{-1})
1	Ag	R	19
2	Ag	R	37
3	Ag	R	51
4	Ag	R	76
5	Au	IR	79
6	Au	IR	87
7	Ag	R	87
8	Ag	R	99
9	Au	IR	99
10	Ag	R	115
11	Ag	R	116
12	Ag	R	118
13	Au	IR	120
14	Au	IR	133
15	Au	IR	135
16	Au	IR	142
17	Ag	R	152
18	Au	IR	159
19	Ag	R	162
20	Au	IR	162
21	Au	IR	165
22	Ag	R	186
23	Ag	R	197
24	Au	IR	216
25	Au	IR	222
26	Ag	R	225
27	Ag	R	278

Table E2. Γ-point frequencies calculated for Ag_6Cl_4 at DFT-D3. Irrep – irreducible representation, IR – infrared active, R – Raman active.

Mode no.	**Irrep**	**Optical activity**	**E (cm^{-1})**
1	Ag	R	20
2	Ag	R	39
3	Ag	R	57
4	Ag	R	80
5	Au	IR	83
6	Au	IR	92
7	Ag	R	95
8	Ag	R	103
9	Au	IR	105
10	Ag	R	116
11	Ag	R	120
12	Ag	R	122
13	Au	IR	124
14	Au	IR	138
15	Au	IR	142
16	Au	IR	152
17	Ag	R	163
18	Au	IR	165
19	Au	IR	171
20	Au	IR	173
21	Ag	R	174
22	Ag	R	193
23	Ag	R	201
24	Au	IR	224
25	Au	IR	226
26	Ag	R	237
27	Ag	R	286