MOLECULAR PHYSICS

Supplemental Material for "Bonding in the Metallic Molecular Solid α-Gallium"

Richard C. Remsing[a]*, Jianwei Sun[b], Umesh V. Waghmare[c], and Michael L. Klein[a]*

[a] Institute for Computational Molecular Science and Department of Chemistry, Temple University, Philadelphia, PA 19122, USA, [b]Department of Physics and Engineering Physics, Tulane University, New Orleans, LA 70118, [c]Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

The work in the main text is performed with the `CP2K` package [1], which employs basis sets of Gaussian-type orbitals and plane waves for the electron density. To verify the proposed limitations of the basis sets available for Ga, we performed additional calculations with the purely plane wave code VASP [2]. We find that convergence of the lattice parameters is achieved with a cutoff of $E_{cut} = 250$ eV and a $14 \times 14 \times 14$ k-point grid for the unit cell of α-Ga. Optimized lattice parameters and atomic volumes for α-Ga are listed in Tables 1 from SCAN [3], LDA, and experimental measurements, as well as the additional functionals PW91 [4], PBE [5], and PBE-sol [6]. We also performed calculations using both LDA- and PBE-based pseudopotentials with SCAN. We find that SCAN provides the best estimate of the unit cell of α-Ga among the functionals studied. Moreover, we find that the results are relatively insensitive to the pseudopotential, although the pseudopotentials are both ultrasoft; switching to a hard pseudopotential may further impact the results. This suggests that the gallium basis sets available for use with CP2K may not be accurate for describing pure Ga phases with SCAN, and new SCAN-based basis sets need to be developed, as discussed in the main text.

Table 1. Lattice parameters and specific volume obtained for α-Ga from different exchange-correlation (XC) functionals and experiments. For SCAN, different pseudopotentials are indicated in parentheses.

XC	a (Å)	b (Å)	c (Å)	V/N (Å^3)
SCAN (LDA)	4.474	7.635	4.527	19.330
SCAN (PBE)	4.477	7.640	4.530	19.368
PW91	4.586	7.731	4.585	20.320
PBE	4.580	7.744	4.588	20.341
PBE-sol	4.477	7.595	4.490	19.084
LDA	4.420	7.496	4.440	18.388
Expt.	4.5192	7.6586	4.5258	19.58

RCR: rremsing@temple.edu
MLK: mike.klein@temple.edu

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