

First-principles study of the connection between structure and electronic properties of gallium

Elena Voloshina,^{1,*} Krzysztof Rosciszewski,^{2,3} and Beate Paulus¹¹Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany²Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany³Institute of Physics, Jagiellonian University, Reymonta 4, 30059 Krakow, Poland

(Received 11 September 2008; revised manuscript received 25 November 2008; published 20 January 2009)

Different structures of gallium have been studied by means of density-functional theory. The density of states of orthorhombic α -Ga, the only elemental solid exhibiting both metallic and molecular characters at zero pressure, shows a pseudogap at the Fermi energy. Complex analysis of the relation between lattice structure and the corresponding electronic properties allows us to throw light upon an origin of the pseudogap. We have found that the free-electron-like behavior which is a property of the high-pressure bct and fcc phases of gallium depends strongly on the arrangement of atoms in the buckled planes, one of the building blocks of the orthorhombic gallium.

DOI: 10.1103/PhysRevB.79.045113

PACS number(s): 71.15.-m, 71.30.+h, 61.50.Lt

I. INTRODUCTION

The group 3 elements occupy a unique position in the periodic table since they are situated at the borderline between metallic bonded elements and the covalently bonded ones. Being the subject of the present study, Al, Ga, and In demonstrate different ground-state structures at ambient conditions. Aluminum crystallizes in the simple face-centered-cubic (fcc) structure with lattice constant of 4.05 Å.¹ Indium condenses in a body-centered-tetragonal (bct) structure ($a = 3.25$ Å and $c = 4.94$ Å),¹ which corresponds to distorted fcc arrangements in which the environment of 12 nearest neighbors is split into two sets of atoms (Fig. 1). The c/a ratio is 1.52 and thus larger than that for the ideal case of fcc structure ($\sqrt{2}$). For Al and In no structural changes are observed up to high pressure (220 and 67 GPa for Al and In, respectively²).

Gallium has one of the most complicated phase diagrams among all elemental metals. At ambient pressure and room temperature, Ga crystallizes in the orthorhombic α phase (Ga-I) with eight atoms in the conventional unit cell¹ [Fig. 2(a)]. Additionally, several metastable phases have been observed. At a compression of 2 GPa and room temperature,

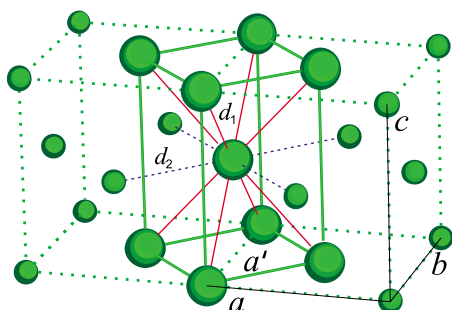


FIG. 1. (Color online) Structural relation between the fcc and bct structures. Two fcc unit cells are shown (indicated with dotted lines). bct unit cell is depicted with thick solid lines. In the fcc $a = b = c$ and as a consequence $d_1 = d_2$, i.e., the central atom has 12 nearest neighbors. In the bct the environment of 12 nearest neighbors is split into two sets of atoms indicated as eight large spheres and four small spheres ($d_1 < d_2$).

gallium forms the metastable Ga-III phase,³ which has a simple bct structure. The highly complex Ga-II phase is obtained when Ga-I is compressed at temperature below 273 K, or when metastable Ga-III is supercooled down to 200 K at pressures around 3 GPa.³ The Ga-II phase crystallizes with a 104-atom orthorhombic structure.⁴ Further room-temperature compression transforms Ga-II into the Ga-V phase with a rhombohedral structure.⁴ Above 14 GPa the bct Ga-III phase is stabilized. At even higher pressure (about 120 ± 10 GPa) Ga finally undergoes a transition to the fcc structure (Ga-IV).⁵ Due to its peculiar behavior under pressure, Ga metal has been the subject of much attention for decades.³⁻¹⁵

The Ga-I \rightarrow Ga-III transition shows some remarkable features. The ground-state structure exhibits both molecular and metallic characters because of the coexistence of strong Ga-Ga covalent bonds formed by the nearest-neighbor (NN) atoms [see Fig. 2(a), where the corresponding Ga dimers are shown with dashed lines]. As a consequence the electronic density of states (DOS) has a pseudogap at the Fermi energy

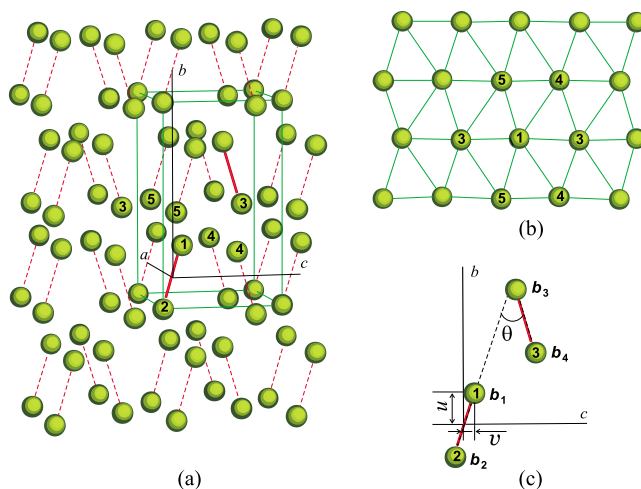


FIG. 2. (Color online) (a) Crystallographic structure of α -Ga [D_{2h}^{18} space group]: seven nearest neighbors are marked with numbers (the larger number corresponds to the longer distance from the atom 1); (b) strongly buckled plane containing atoms 1, 3, 4, and 5 (cf. text); (c) explanation of parameters u , v , and θ (cf. text).

TABLE I. CRYSTAL-optimized Gaussian basis sets for Al (all electrons), Ga (21 valence electron pseudo-potentials), and In (21 valence electron pseudopotentials).

Al			Ga:Ga ²¹⁺ -PP			In:In ²¹⁺ -PP		
<i>s</i> exponent	Coefficient	Coefficient	<i>s</i> exponent	Coefficient	Coefficient	<i>s</i> exponent	Coefficient	Coefficient
64 150.000 000	0.000 290	-0.000 076	2 848.200 000	0.000 362	-0.000 097	265.131 000	0.000 770	-0.000 230
9 617.000 000	0.002 251	-0.000 582	420.664 000	0.002 117	-0.000 614	25.569 400	-0.052 791	0.014 088
2 189.000 000	0.011 646	-0.003 081	29.811 800	0.118 964	-0.031 069	16.004 100	0.259 343	-0.078 615
620.500 000	0.046 738	-0.012 311	14.220 700	-0.461 723	0.126 784	6.818 850	-0.739 289	0.252 864
202.700 000	0.146 299	-0.041 978	2.676 430	0.751 559	-0.264 288			
73.150 000	0.330 283	-0.103 371	1.133 530	0.447 202				
28.550 000	0.415 861	-0.196 308						
11.770 000	0.189 253	-0.083 000						
3.300 000	1.000 000		1.335 30	1.000 000		1.666 760	1.000 000	
1.173 000	1.000 000		0.180 00	1.000 000		0.769 232	1.000 000	
0.145 000	1.000 000					0.140 000	1.000 000	
<i>p</i> exponent	Coefficient	Coefficient	<i>p</i> exponent	Coefficient	Coefficient	<i>p</i> exponent	Coefficient	Coefficient
258.800 000	0.004 068		109.624 000	0.002 101	-0.000 288	14.469 100	0.090 177	
60.890 000	0.030 682		21.085 500	-0.080 196	0.013 555 0	9.280 830	-0.267 642	
19.140 000	0.129 149		4.922 600	0.396 415	-0.073 629			
6.881 000	0.320 831		2.155 910	0.519 076	-0.120 860			
			0.901 910	0.207 520				
2.547 000	1.000 000		0.901 910	1.000 000		2.082 010	1.000 000	
0.957 000	1.000 000		0.170 000	1.000 000		0.844 314	1.000 000	
0.175 000	1.000 000					0.150 000	1.000 000	
<i>d</i> exponent	Coefficient	Coefficient	<i>d</i> exponent	Coefficient	Coefficient	<i>d</i> exponent	Coefficient	Coefficient
			85.797 800	0.014 668		30.787 900	0.005 766	
			27.682 200	0.085 621		19.255 500	-0.010 708	
			10.176 000	0.248 336		3.196 620	0.293 860	
			3.922 080	0.401 414		1.332 100	0.510 869	
			1.458 580	0.398 604				
0.750 000	1.000 000		0.488 760	1.000 000		0.504 619	1.000 000	
0.150 000	1.000 000		0.180 000	1.000 000		0.140 000	1.000 000	

(E_F).^{6,7} On the other hand, bct Ga as well as fcc Ga show nearly free-electron behavior.⁵

In this paper we present a detailed investigation of the connection between structural and electronic properties of gallium. In order to estimate the influence of electron correlation effects on the electronic structure of Ga-I, we compared Hartree-Fock (HF) results with those of density-functional theory (DFT) calculations. Another purpose of the present study is to find a structural quantity which is responsible for the unusual DOS of the orthorhombic gallium.

The paper is organized as follows: In Sec. II we present CRYSTAL-optimized contracted Gaussian-type basis sets of valence-double- ζ quality for the group 3 elements Al, Ga, and In, and the technical details of our calculations. Then (see Sec. III), in order to deduce valuable details of the binding properties of Al, Ga, and In, we compared HF results for

the ground-state properties of these metals with those of DFT calculations as well as both with the corresponding experimental data. Influence of different structural parameters (such as distance between neighboring atoms, angle between dimers (θ), and coordination number) on the behavior of the electronic states of gallium has been investigated. Discussion of the obtained results can be found in Sec. IV. Conclusions follow in Sec. V.

II. COMPUTATIONAL DETAILS

We performed periodic mean-field calculations for bulk Al, Ga, and In using the program package CRYSTAL06.¹⁶ In order to obtain converged results for the HF binding energy, we changed the default parameters: the following tolerances

were employed in the evaluation of the infinite Coulomb and HF exchange series: 10^{-9} for the Coulomb overlap and penetration as well as for exchange overlap and the first exchange pseudo-overlap and 10^{-15} for the second exchange pseudo-overlap. We chose a Pack-Monkhorst k -point mesh with an isotropic shrinking factor of 12 (i.e., 12 k points along each of the three dimensions in reciprocal space), and for the Gilat k point net (needed in conducting systems), a shrinking factor of 24. In this work we have made use of an all-electron description in the case of Al. The chemically inactive [Ne] or [Ar] $3d^{10}$ cores of the Ga and In atoms, respectively, were simulated by energy-consistent scalar-relativistic pseudopotentials: Ga $^{21+}$ -PP and In $^{21+}$ -PP.¹⁷ Basis sets designed for free atoms and molecules have to be modified to be used in a crystal. Usually the procedure is as follows: the inner contractions of the atomic orbitals are kept unchanged because the inner electronic shells in free atoms will not be very different from those in the solid. On the other hand the most diffused outer exponents, which are necessary for the free atoms, must be neglected in the solid because, due to the dense packing in the solid, basis functions on the neighboring atoms will take over their part. The basis sets used are contracted Gaussian-type orbital sets obtained from the correlation consistent polarized valence

double zeta (cc-pVDZ) basis sets.^{18,19} In order to construct a basis set suitable for the periodic metal, we left out the outermost sp exponents, decontracted the sp exponents in the range between 0.1 and 2, and reoptimized two sp exponents as well as two d exponents in this range (Table I). For Al two d -type polarization functions have been introduced. The modification was done in order to minimize the total energy per unit cell while maintaining SCF stability.

In order to test the quality of our basis set, we performed a series of calculations making use of different approximations of DFT, namely, local-density approximation (LDA) (S-VWN: Dirac-Slater exchange, Vosko-Wilk-Nusair correlation²⁰) and generalized gradient approximation (GGA) [Perdew-Wang (PW91) exchange and correlation²¹ as well as Perdew-Burke-Ernzerhof (PBE) exchange and correlation²²], as well as two hybrid functionals with mixed Hartree-Fock (20%) and DFT exchange and correlation [B3LYP and B3PW (Refs. 21, 23, and 24)]. The HF (or DFT) energy of the free atom is corrected for the basis set superposition error (BSSE) by a counterpoise correction.²⁵ The atomic energy is calculated with the optimized crystal basis set in the presence of the same basis sets placed at the positions of neighboring atoms in the solid (convergence required two shells of nearest neighbors). The quantum-

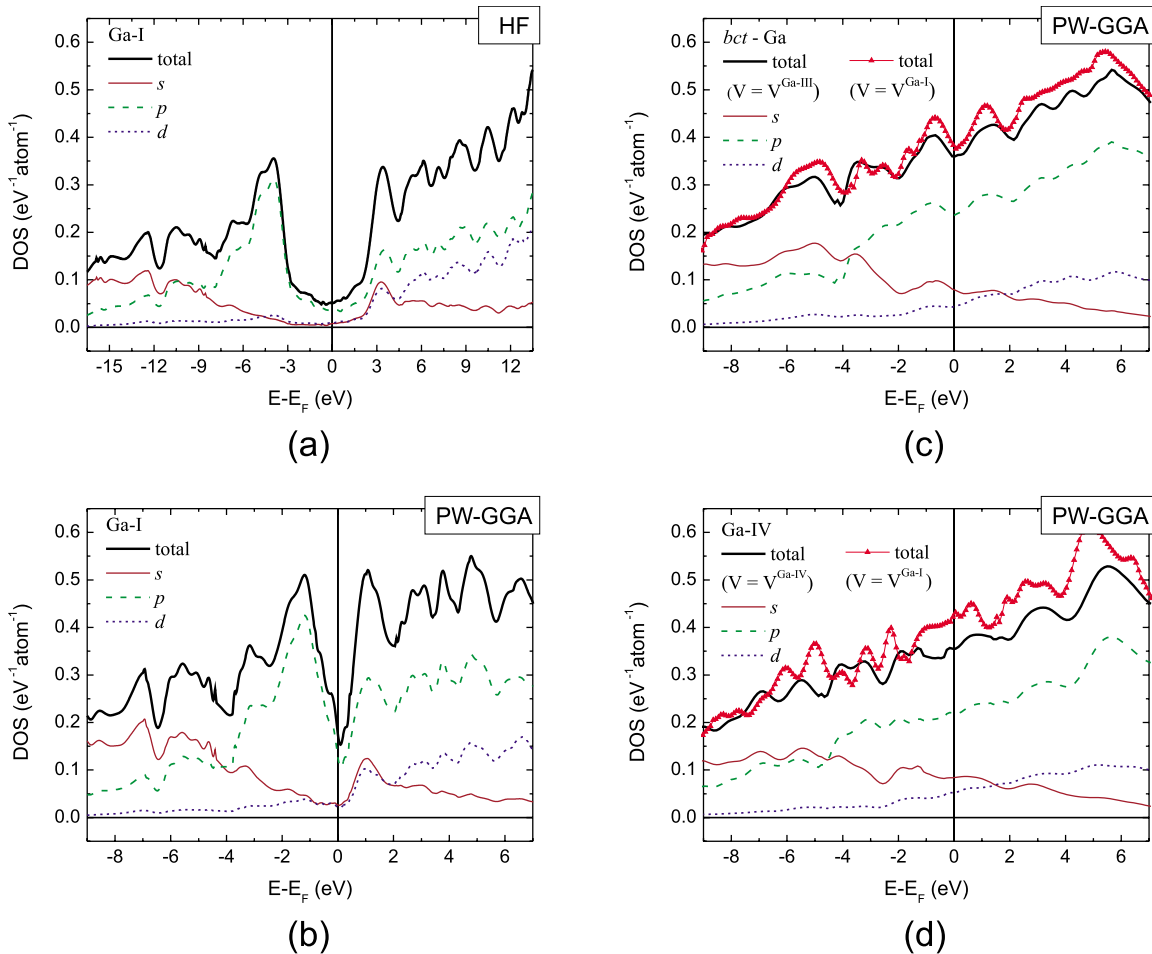


FIG. 3. (Color online) Total and partial densities of states of Ga: (a) as obtained at HF level for the orthorhombic Ga (Ga-I), (b) as obtained with PW-GGA functional for the orthorhombic Ga (Ga-I), (c) as obtained with PW-GGA functional for the bct structure of Ga (Ga-III), and (d) as obtained with PW-GGA functional for the fcc structure of Ga (Ga-IV).

TABLE II. Cohesive energies (in eV) of Al, Ga, and In as calculated for the different lattice structures.

	Al			In		Ga		
	fcc	orthorhombic ^a	bct	fcc ^a	orthorhombic ^a	orthorhombic	fcc ^a	bct ^a
Expt. ^b	-3.39		-2.52			-2.81		
HF	-1.43	-1.51	-0.63	-0.65	-1.06	-1.51	-0.88	-0.84
LDA	-4.02	-3.74	-3.10	-3.09	-3.11	-3.61	-3.42	-3.43
PBE	-3.42	-3.11	-2.38	-2.38	-2.34	-2.87	-2.72	-2.72
PWGGA	-3.48	-3.13	-2.35	-2.34	-2.30	-2.87	-2.72	-2.73
B3LYP	-2.51	-2.36	-1.68	-1.67	-1.74	-2.25	-1.98	-1.99
B3PW	-3.17	-2.90	-2.10	-2.09	-2.12	-2.64	-2.42	-2.42

^aCalculated for the experimental volume (cf. text).

^bReference 1.

chemical *ab initio* program system MOLPRO 2006 (Ref. 26) was used for the atomic calculations.

III. GROUND-STATE PROPERTIES

The cohesive energy per unit cell is defined as $E_{\text{coh}} = E_{\text{tot}} - \sum^N E_a$, where E_a is the atomic energy for each atom belonging to the crystal unit cell and N is the number of atoms in the unit cell. E_{coh} computed for the experimental lattice constant are listed in Table II in comparison with experimental values. For all three elements under examination, common trends have been observed. The HF cohesive energies of the solid Al, Ga, and In by approximately 30%–40% were underestimated with respect to the experimental values. It is a better agreement with $E_{\text{coh}}^{\text{expt}}$ than in the case of the other previously studied group 1, 2, 11, and 12 metals.^{27,28} The LDA values are generally too high. The best agreement with experiment is found for the GGA functional in its PW form. As has been found for some other metals,²⁷ two commonly used hybrid functionals (B3LYP and B3PW) give seriously different (by 20%–30%) results for the cohesive energy.

For aluminum we have studied also mechanical properties, namely, the lattice constant a and bulk modulus, B .²⁹ HF-optimized lattice constant overestimates a^{expt} ($a^{\text{expt}} = 4.05 \text{ \AA}$) (Ref. 1) by about 3%. This is again in better agreement as compared with the data obtained for group 1, 2, and 12 metals.^{27,28} Nevertheless, this slight disagreement yields an underestimation of B^{HF} by about 20%. The DFT-calculated equilibrium lattice constants (4.00–4.10 \AA) are in good agreement with each other and with the experimental values (with deviation of 1%–2%). The same is true also for the calculated bulk moduli (62–74 GPa) with the exception of B3LYP value (51.8 GPa) which is about 30% lower than the measured B ($B^{\text{expt}} = 76.0 \text{ GPa}$). The latter is the consequence of the underestimation of electron correlation effects by this functional, which can be clearly seen when considering both the very low value of cohesive energy and the rather long lattice constant.

In Table II we list also the values for Al, In, and Ga, calculated for the experimental volume (i.e., $16.61 \text{ \AA}^3/\text{atom}$ for Al, $26.14 \text{ \AA}^3/\text{atom}$ for In, and $19.35 \text{ \AA}^3/\text{atom}$ for Ga) for different lattice structures. In order to generate an ortho-

rhombic lattice for Al and In, we have used the corresponding covalent radii values: $r_{\text{Al}} = 1.21 \text{ \AA}$ and $r_{\text{In}} = 1.42 \text{ \AA}$.³⁰ This yields the following coordinates of the atomic position within the orthorhombic D_{2h}^{18} symmetry group: (0.0; 0.1597; 0.0822) and (0.0; 0.1610; 0.0829) for Al and In, respectively. When comparing the obtained E_{coh} of Al, one notes that the orthorhombic structure is more stable at HF level than the experimentally determined one. This is due to overestimation of the covalent character by HF and is similar for the three studied systems. Including the effect of correlations changes

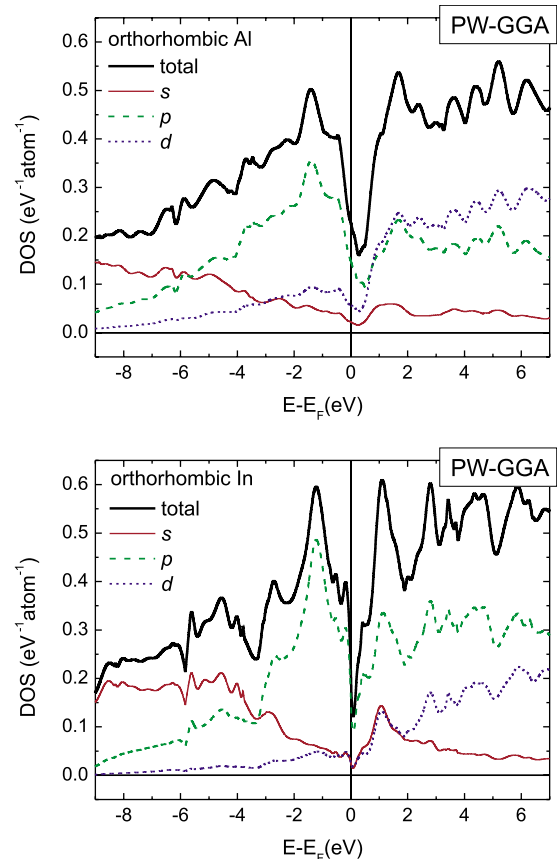


FIG. 4. (Color online) Total and partial densities of states of orthorhombic Al (upper panel) and In (lower panel) as obtained by means of DFT (PW-GGA exchange and correlation functionals).

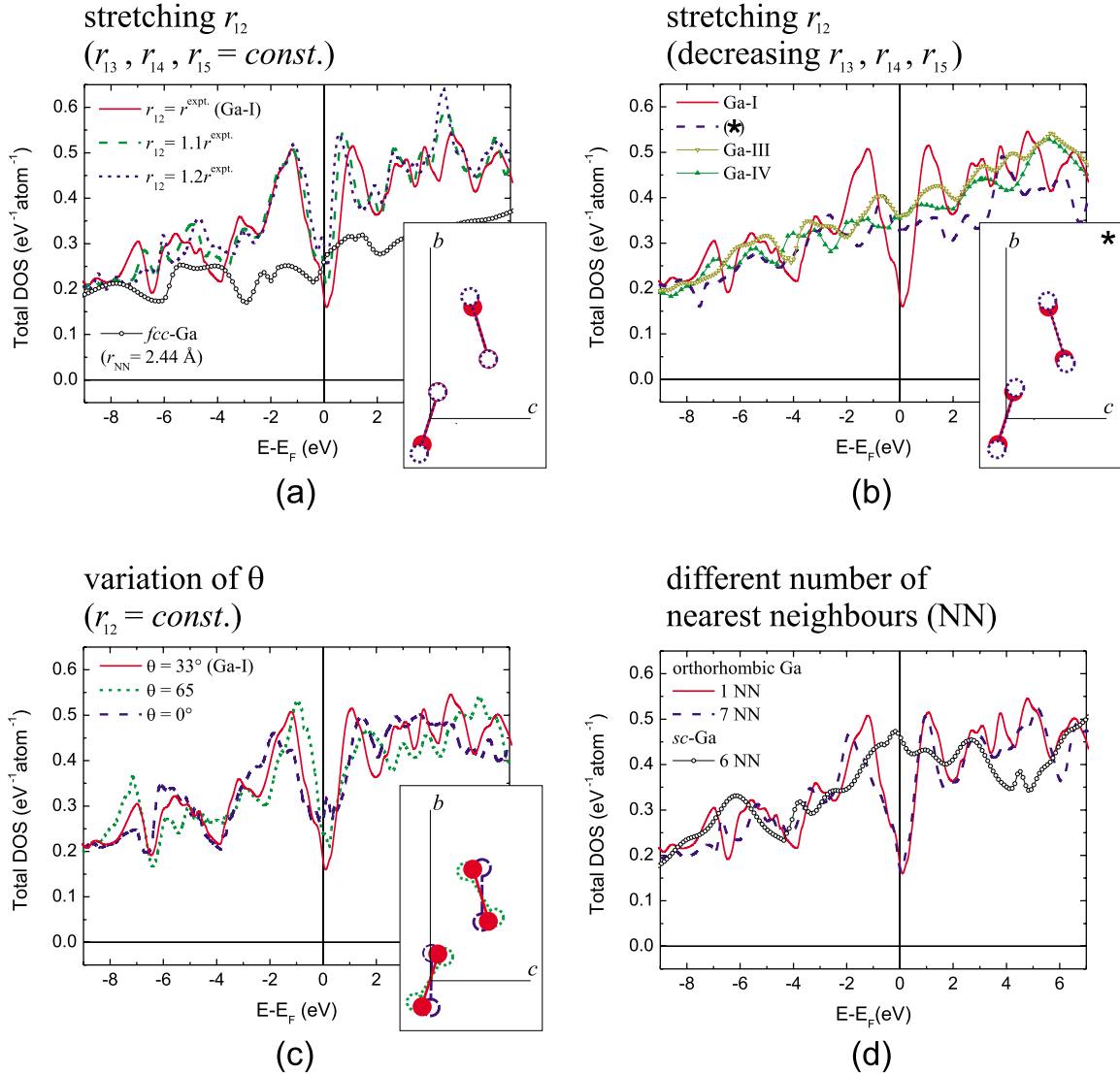


FIG. 5. (Color online) Total density of states obtained for (a) the orthorhombic Ga when stretching interdimer distance r_{12} ($a, c, r_{13}, r_{14}, r_{15}$, and θ were set to experimental values) in comparison with the fcc Ga ($r_{NN}=2.44 \text{ \AA}$), (b) the orthorhombic Ga when stretching interdimer distance r_{12} (a, b, c , and θ were set to experimental values) in comparison with Ga-III and Ga-IV, (c) the orthorhombic Ga when varying angle between dimers θ (a, b, c, r_{12} were set to experimental values), and (d) the orthorhombic Ga when coordination number of Ga is one (solid line) and seven (dashed line) in comparison with the sc Ga, where coordination number is six.

this preference in the case of Al: all considered DFT functionals show the fcc structure to be more stable. Surprisingly, fcc and bct structures are equivalently favorable for In at all levels of theory. However, difference in volume between these two structures can determine the ground-state one. The situation with the orthorhombic In is not clear since some DFT functionals, namely, LDA and the two hybrid ones, predict the orthorhombic structure to be more stable than the ground-state one. In contrast, the GGA functionals give correct sequence of energies in this case. For Ga, fcc and bct structures are obviously energetically less favorable than the orthorhombic one, which is in agreement with experiment.

IV. NATURE OF A PSEUDOGAP IN THE DOS OF THE ORTHORHOMBIC GALLIUM

The α phase of gallium (Ga-I), which is the most stable at atmospheric pressure and 0 K, is a complicated orthorhombic

lattice, which is the same structure as that of the solid halogens Cl_2 , Br_2 , and I_2 . In this unusual metallic structure each gallium atom has only one NN at a distance of 2.44 \AA , and six other neighbors between 2.71 and 2.80 \AA . These six atoms can be seen as lying on a distorted (strongly buckled) plane [Fig. 2(b)] about 1.9 \AA thick, perpendicular to the $\langle 010 \rangle$ direction. The bonding between the nearest neighbors is found to be of covalent character; hence Ga_2 dimers are seen as the fundamental building blocks of the crystal [indicated with dashed lines in Fig. 2(a)]. Taking this in mind, one can predict the partial covalent character of α -Ga.⁸ Indeed, the electronic DOS derived from a photoemission experiment on polycrystalline α -Ga shows a broad maximum of 1.2 eV below E_F and an unusually steep decrease toward E_F , suggesting a pseudogap.⁶

In addition to the lattice constants ($a=4.49 \text{ \AA}$, $b=7.63 \text{ \AA}$, and $c=4.52 \text{ \AA}$), there are two parameters u

$=0.1525$ and $v=0.0785$ which are necessary in specifying positions of the atoms in the unit cell. They are given by vectors

$$\mathbf{b}_1 = ub\mathbf{j} + vck,$$

$$\mathbf{b}_2 = -ub\mathbf{j} - vck,$$

$$\mathbf{b}_3 = \left(\frac{1}{2} + u\right)b\mathbf{j} + \left(\frac{1}{2} - v\right)ck,$$

$$\mathbf{b}_4 = \left(\frac{1}{2} - u\right)b\mathbf{j} + \left(\frac{1}{2} + v\right)ck,$$

where \mathbf{j} and \mathbf{k} are unit vectors along y and z axes. It can be clearly seen [Fig. 2(b)] that, by varying u and v , one changes positions of atoms, modifying thereby the angle θ between dimers [Fig. 2(b)]: $\cos \theta = (u^2b^2 - v^2c^2)/(u^2b^2 + v^2c^2)$. This modification yields change in distances between neighboring atoms. Therefore, finally the orthorhombic structure of gallium may be described by eight parameters (numbers in parentheses correspond to experimentally observed values): the lattice constants a , b , and c , the four interatomic distances r_{12} (2.44 Å), r_{13} (2.71 Å), r_{14} (2.74 Å), and r_{15} (2.80 Å), and the angle θ (33°) between dimers.

The DFT-calculated density of states of orthorhombic Ga [PW-GGA functional, Fig. 3(b)] is in good agreement with experimentally and theoretically obtained previously published data.⁵⁻⁸ Note that other types of functionals predict nearly identical electronic structure of α -Ga. In order to estimate the influence of electron correlation effects on the electronic structure of Ga metal, we presented here DOS calculated for orthorhombic Ga as obtained at HF level [Fig. 3(a)]. The pseudogap can be observed already when considering HF data; however at DFT-calculated DOS it is less pronounced. That is a typical picture when comparing HF (overestimates the gap) and DFT (underestimates the gap) results. This comparison allows us to conclude that, although electronic correlations are important for the detailed shape of the DOS, the pseudogap occurs for HF as well as for the correlated methods. The wider pseudogap in the case of HF calculated DOS is a consequence of overestimation of the covalent character by this method (see Sec. III). For further comparison we calculated DOSs for the bct as well as fcc modifications of Ga (Ga-III and Ga-IV, respectively). The results are presented in Figs. 3(c) and 3(d). The free-electron-like behavior of the electronic states is a characteristic of both phases. This is in good coincidence with data published in Ref. 5. In order to estimate the influence of changes in volume, we present here also results obtained for bct and fcc Ga adopting volume of the orthorhombic phase [Figs. 3(c) and 3(d); $V=V^{\text{Ga-I}}$]: one observes only insignificant changes for the two studied cases.

In order to understand whether the pseudogap observed in the DOS of the orthorhombic Ga is specific to this element, we performed the corresponding calculations for the orthorhombic Al and In (see Sec. III). The results are presented in Fig. 4. One can clearly see the similar character of DOS in both cases. This gives an additional clue that the nature of

particular behavior of Ga is that the metal forms a stable orthorhombic structure. The same picture could be observed for its isoelectronic elements if such type of crystals were energetically favorable in those cases.

As has been mentioned above, the pseudogap occurring in the DOS of Ga-I can be viewed as a consequence of the partial covalent character caused by comparatively short distances between NN atom pairs. In order to find quantitative confirmation for this point of view, we fixed a , c , r_{13} , r_{14} , r_{15} , and θ at experimental values and increased b . This yields a stretching of r_{12} . When looking in Fig. 5(a), one notes that, even at $r_{12}=1.2r_{12}^{\text{expt}}$, which is even longer than the nearest-neighbor distance in fcc Ga (2.83 Å), the behavior of the electronic states remains nearly unchanged. Thus, the covalent distance between the two nearest neighbors in the orthorhombic lattice is not the most important structural quantity provoking the pseudogap. An additional support to this conclusion can be the result for the fcc Ga with $a=3.45$ Å [i.e., $r_{\text{NN}}=2.44$ Å, see Fig. 5(a)]. There the free-electron-like character of electronic states can be clearly seen. At the same time, setting b to the experimental value ($b=\text{const}$) and

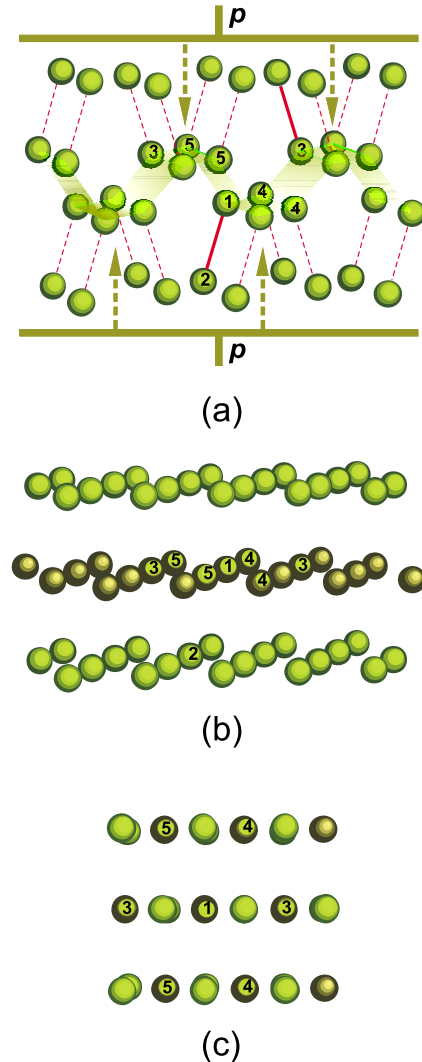


FIG. 6. (Color online) [(a) and (b)] Possible behavior of the orthorhombic Ga upon compression; (c) top view of structure (b).

stretching r_{12} leads to flattening of the buckled planes (decreasing r_{13} , r_{14} , and r_{15}). In this case one can observe significant change in the character of DOS [Fig. 5(b)].

All described above calculations have been performed at fixed θ . Now we want to check whether changing the angle between dimers makes any difference for the studied property. However, during such manipulations with dimers, one has to exclude the situation when distances between neighboring Ga atoms become too short (here we mean r_{13} , r_{14} , and r_{15} since $r_{12}=\text{const}$). The DOSs calculated for the two extreme cases, namely, $\theta=0^\circ$ and 63° , are presented in Fig. 5(c). One can see somewhat smaller pseudogap compared with the picture of Ga-I, especially in the case when two dimers are parallel, which can be relevant to rather strong decrease in r_{15} (flattening of the distorted plane).

One more factor that can affect the DOS is the coordination number of Ga. In Ga-I each atom has only one NN at distance $r_{12}=2.44$ Å. In the high-pressure modifications Ga-III and Ga-IV, the coordination number of Ga is 8 and 12, respectively. Without changing of lattice constants a , b , and c as well as angle θ , one can modify u and v in such a way that each Ga will have three NNs (namely, setting $u=0.1638$ and $v=0.08432$). It is possible even to increase the number of NN atoms to 7 by slight (about 5%) compression of the lattice along $\langle 100 \rangle$ direction (setting $a=4.265$ Å). One can note when looking in Fig. 5(d) that this rearrangement has nearly no effect on general behavior of the electronic states of gallium.

The aforesaid observations help us to make a step toward understanding the orthorhombic-to-bct structural transition that can take place in Ga under high pressure. Due to strong

covalent character of the bond between Ga¹ and Ga² (short r_{12} distance), only distances r_{13} , r_{14} , and r_{15} are expected to decrease upon compression. This yields a flattening of the strongly buckled plane to a planar one based on the atoms 1, 3, 4, and 5. In this case the Ga atoms are arranged in a bct-like structure (Fig. 6).

V. CONCLUSION

We performed DFT study of structural and electronic properties of Ga-I (orthorhombic) and its high-pressure modifications Ga-III (bct) and Ga-IV (fcc). The lattice structure of orthorhombic Ga may be viewed as consisting of distorted planes connected by dimers. A detailed analysis of the structural quantities in connection with the corresponding electronic properties allows us to conclude that arrangement of atoms in the buckled planes influences strongly on the electronic properties of gallium. It has been shown that flattening of these planes can yield a free-electron-like behavior of the electronic states. The presented results can be further used for explanation of the mechanism of transitions in gallium.

ACKNOWLEDGMENTS

E.V. acknowledges gratefully the financial support by DFG Priority Program under Contract No. 1145 ("Modern and universal first-principles methods for many-electron systems in chemistry and physics"). E.V. thanks Yu. S. Dedkov (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin) for useful discussions.

*Corresponding author; velen@chemie.fu-berlin.de

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