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Item Type	Article
Authors	Zhu, Zhiyong;Schwingenschlög, Udo;Wang, Xuhui
Citation	Zhu Z, Wang X, Schwingenschlög U (2011) Role of electronic correlations in Ga. Appl Phys Lett 98: 241902. doi:10.1063/1.3599532.
Eprint version	Publisher's Version/PDF
DOI	10.1063/1.3599532
Publisher	AIP Publishing
Journal	Applied Physics Letters
Rights	Archived with thanks to Applied Physics Letters
Download date	2023-12-01 10:35:30
Link to Item	http://hdl.handle.net/10754/314508

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Citation: *Applied Physics Letters* **98**, 241902 (2011); doi: 10.1063/1.3599532

View online: <http://dx.doi.org/10.1063/1.3599532>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/98/24?ver=pdfcov>

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Role of electronic correlations in Ga

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(Received 2 May 2011; accepted 23 May 2011; published online 13 June 2011)

An extended around mean field (AMF) functional for less localized p electrons is developed to quantify the influence of electronic correlations in α -Ga. Both the local density approximation (LDA) and generalized gradient approximation are known to mispredict the Ga positional parameters. The extended AMF functional together with an onsite Coulomb interaction of $U_{\text{eff}} = 1.1$ eV, as obtained from constraint LDA calculations, reduces the deviations by about 20%. The symmetry lowering coming along with the electronic correlations turns out to be in line with the Ga phase diagram. © 2011 American Institute of Physics. [doi:10.1063/1.3599532]

Electronic correlations beyond the local density and generalized gradient approximation (LDA/GGA) to density functional theory (DFT) are usually considered to be exclusive to partially filled d and f states.¹⁻⁴ The localized nature of these orbitals results in a non-negligible onsite Coulomb interaction U .⁵⁻⁹ The importance of correlations in partially filled p orbitals recently has been pointed out in the context of “ d^0 magnetism,” where the magnetic order arises from the p states instead of the conventional d and f states.^{10,11} First-principles calculations have shown that correlations in open p shells exist not only for first-row elements, like N and O ($2p$), but also for heavier atoms, like Te ($5p$).^{12,13} Up to now, the interest in p orbital electronic correlations was limited to pure and doped ionic semiconductors.

Great interest in α -Ga was triggered by the common belief that it is the only elemental solid in which metallicity and covalency coexist.¹⁴ Showing orthorhombic crystal symmetry with space group $Cmca$, α -Ga is the most stable Ga phase at ambient conditions.^{15,16} Besides the lattice constants $a=4.5102$ Å, $b=4.5161$ Å, and $c=7.6448$ Å, the crystal structure is determined by the two internal parameters $u=0.0785$ and $v=0.1525$, which specify the Ga atomic positions in the unit cell.¹⁷ Every Ga atom (Ga_{ref} in Fig. 1) has one nearest neighbor (Ga_1) and six neighbors in the next three coordination shells (Ga_2 to Ga_4). Partial covalency of α -Ga, indicated by the short $\text{Ga}_{\text{ref}}-\text{Ga}_1$ bond, highly anisotropic electronic and thermal conductivities, and a steep pseudogap around the Fermi level have been observed in experiments¹⁸⁻²² and LDA/GGA calculations.^{14,17,23} The different bond lengths between Ga_{ref} and Ga_i ($i=1,2,3,4$) constitute a special local environment, which is crucial to the coexistence of metallicity and covalency in α -Ga. As it is reported in Ref. 17 and confirmed by our calculations, however, the LDA/GGA fails miserably to reproduce the experimental Ga positional parameters. It is our aim to evaluate to which extent electronic correlations account for this deficiency.

The standard way to treat electronic correlations in a DFT calculation is to consider an onsite parameter U and to embed a Hubbard-like Hamiltonian into the LDA/GGA Kohn–Sham equations (LDA/GGA+ U method).² However, usually the onsite U is applied only to the electrons inside the nonoverlapping muffin-tin spheres. By the neglect of ef-

fects from the interstitial electrons, any result will depend on the muffin-tin radius R_{mt} . Major inaccuracies are expected for more delocalized states, like the $4p$ electrons of α -Ga. As a consequence, an extended LDA/GGA+ U functional is required which includes the effects of the interstitial charge. Due to the reduced localization of the p electrons, a less strongly correlated state is expected. Hence, the around mean field (AMF) approximation is chosen for modeling α -Ga.^{2,24}

Based on the fact that the LDA corresponds to the homogeneous solution of the mean field Hartree–Fock equations with equal occupancy of all suborbitals with the same spin, the AMF energy functional is obtained by supplementing the LDA/GGA functional by the additional term^{2,4}

$$E^{\text{AMF}} = -\frac{U_{\text{eff}}}{2} \sum_{\sigma} \text{Tr}(\mathbf{n}_{\sigma} - \bar{n}_{\sigma} \mathbf{I})^2. \quad (1)$$

In this relation $U_{\text{eff}}=U-J$ is the effective interaction, where U and J denote the onsite Coulomb and exchange interactions, respectively, and \mathbf{n}_{σ} the density matrix for spin σ . In addition, $\bar{n}_{\sigma}=\text{Tr}(\mathbf{n}_{\sigma})/(2\ell+1)$ is the average occupation num-

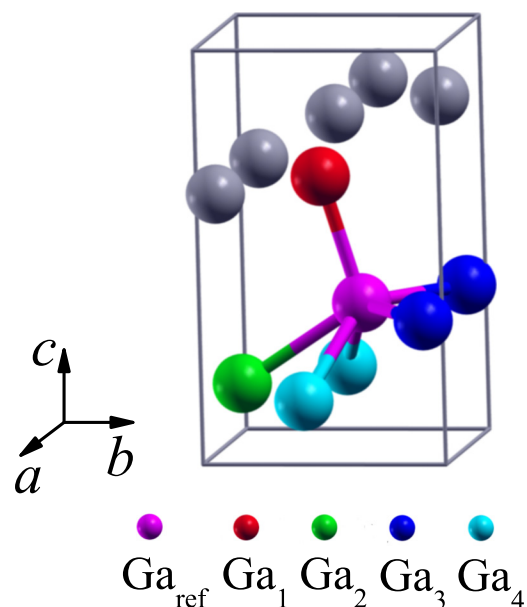


FIG. 1. (Color online) Local environment of a reference atom Ga_{ref} . Ga_i ($i=1,2,3,4$) denotes the atoms in the i th coordination shell of Ga_{ref} . Notice that there are two Ga_2 atoms due to the periodicity along the b -axis.

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TABLE I. Fully optimized structural parameters (a , b/a , c/a , u , and v) of α -Ga obtained from standard LDA/GGA calculations. Different XC functionals, including (1) LDA-PW92, (2) GGA-SOGGA, (3) GGA-AM05, (4) GGA-PBESol, (5) GGA-WC, (6) GGA-PBEalpha, (7) GGA-PBE, (8) GGA-PW91, (9) GGA-BPW91, and (10) GGA-RPBE, are used (Ref. 24). The experimental values are taken from Ref. 17.

	a (Å)	b/a	c/a	u	v	δVol (%)
Expt.	4.5102	1.695	1.0013	0.0785	0.1525	0
(1)	4.4262	1.695	1.0014	0.0843	0.1559	-5.48
(2)	4.4378	1.705	1.0074	0.0821	0.1558	-3.59
(3)	4.4646	1.703	1.0064	0.0815	0.1561	-2.03
(4)	4.4658	1.703	1.0064	0.0829	0.1559	-1.95
(5)	4.4816	1.698	1.0033	0.0834	0.1559	-1.51
(6)	4.5300	1.698	1.0033	0.0825	0.1561	1.72
(7)	4.5687	1.698	1.0033	0.0803	0.1563	4.34
(8)	4.5743	1.695	1.0013	0.0805	0.1564	4.32
(9)	4.5839	1.695	1.0013	0.0826	0.1562	4.97
(10)	4.6344	1.695	1.0013	0.0808	0.1566	8.48

ber of the suborbitals with spin σ (and orbital quantum number ℓ) and \mathbf{I} the identity matrix. The double counting is already corrected in Eq. (1).

We assume a linear dependence $\mathbf{n}_\sigma = \lambda_\sigma \mathbf{n}_\sigma^{\text{mt}}$ with an orbital dependent parameter λ_σ . Because \mathbf{n}_σ and $\mathbf{n}_\sigma^{\text{mt}}$ can be obtained from the Mulliken method and the DFT calculations, respectively, $\lambda_\sigma = \mathbf{n}_\sigma (\mathbf{n}_\sigma^{\text{mt}})^{-1}$ can be evaluated. For the Mulliken analysis we will apply the Gaussian code.²⁵ In general, λ_σ will depend on the choice of the basis set. However, we have checked a series of basis sets to ensure that the dependence is sufficiently weak. To fix the dependence on R_{mt} , we choose $\text{Tr} \lambda_\sigma / (2l+1) = 2.67$ with $R_{\text{mt}} = 2.2$ a.u. in the following. The (orbital dependent) one-electron potential now is given by the functional derivative of E^{AMF} with respect to $\mathbf{n}_\sigma^{\text{mt}}$,

$$\mathbf{V}_\sigma^{\text{AMF,mt}} = -U_{\text{eff}} \lambda_\sigma (\mathbf{n}_\sigma - \bar{n}_\sigma \mathbf{I}). \quad (2)$$

We have implemented the extended AMF approach, given by Eqs. (1) and (2), for the WIEN2K code.²⁴ Like the original, the modified one-electron potential is applied to this part of a suborbital that is inside the muffin-tin sphere. Yet, there are two improvements. First, the potential exerted by a particular suborbital arises from the Coulomb repulsion of electrons both inside and outside the muffin-tin sphere, $n_{m,\sigma}$, instead of only $n_{m,\sigma}^{\text{mt}}$. Second, the parameter $\lambda_{m,\sigma}$ mimics the energetical effects which would be obtained if both parts of the suborbital (inside and outside the muffin-tin sphere) were subject to the potential, i.e., the extended AMF functional includes effects of charge not only inside the muffin-tin spheres but also in the interstitial region. Thus, it eliminates the dependence of the results on R_{mt} , making it suitable to study electronic correlations in less localized p orbitals.

Using standard LDA/GGA, we have fully optimized the structure of α -Ga against all five structural parameters, applying Pulay corrections to the forces. We use in all calculations $R_{\text{mt}} = 2.2$ a.u., $R_{\text{mt}} K_{\text{max}} = 8.5$, and $l_{\text{max}} = 10$ as well as the same $23 \times 23 \times 14$ k -mesh. The validity of the LDA/GGA is tested for ten exchange-correlation (XC) functionals, see Table I. In order to provide a quantitative comparison between the experimental findings and our results for the unit cell volume (Vol) we study $\delta\text{Vol} = (\text{Vol} - \text{Vol}_{\text{exp}}) / \text{Vol}_{\text{exp}}$. The

TABLE II. Experimental (Refs. 17 and 18) and calculated positional parameters and transport anisotropies.

	Expt.	$U_{\text{eff}}=0$ eV	$U_{\text{eff}}=1.1$ eV
u	0.0785	0.0835	0.0824
v	0.1525	0.1560	0.1556
$\sigma_c : \sigma_b : \sigma_a$	1:3.1:6.7	1:1.8:4.9	1:2.0:5.3
$\kappa_c : \kappa_b : \kappa_a$	1:3.0:6.6	1:2.0:4.4	1:1.8:4.7

a lattice parameter depends strongly on the choice of the XC functional, while both ratios b/a and c/a are almost constant. As a consequence, δVol varies within a wide range from -5.48% to 8.48% . The LDA-PW92 functional yields the smallest value of a and thus the smallest volume, which reflects the common insight that the LDA, in contrast to the GGA, underestimates the volume.^{17,26} The overestimation of u and v in all our data indicates a systematic failure of the LDA/GGA to describe α -Ga. This may be due to the influence of electronic correlations, which we probe in the following.

We apply our extended AMF functional to the outer $4p$ orbitals to optimize the crystal structure, choosing the GGA-WC XC functional for which δVol is minimal. The computational details are the same as in the LDA/GGA calculations. To establish the strength of the onsite Coulomb interaction, we employ the constraint LDA method,²⁷ which leads to $U_{\text{eff}} = 1.1$ eV. With this value and the experimental lattice constants, u and v are optimized in the extended AMF scheme. The anisotropies of the electronic conductivity ($\sigma_c : \sigma_b : \sigma_a$) and the thermal conductivity ($\kappa_c : \kappa_b : \kappa_a$) are obtained,²⁸ see Table II. The extended AMF calculations lead to a qualitative improvement of both the structural and transport properties. Most remarkably, u is improved by about 20% with respect to the experimental value. The extended AMF calculations hence predict a shorter $\text{Ga}_{\text{ref}}\text{-Ga}_1$ bond and a slightly higher anisotropy of the electronic and thermal conductivities, i.e., the partial covalency of α -Ga, which is underestimated by the GGA-WC, is improved. Still, the total and partial s , p_x , p_y , and p_z densities of states (DOS) in Figs. 2(a)–2(e) reveal only little changes.

On the other hand, an enhanced covalency along the c -axis due to the onsite interaction is reflected by the charge density. In Fig. 2(f), we show the charge density difference within the (100) plane, at $x=0.5$, between the GGA-WC and the extended AMF results: $\Delta n = n_{\text{AMF}} - n_{\text{GGA-WC}}$. An accumulation of charge is found in the region between Ga_{ref} and Ga_1 , indicating a stronger $\text{Ga}_{\text{ref}}\text{-Ga}_1$ bond and, thus, an enhanced covalency. The accumulation comes along with charge transfer from the p_x and p_y suborbitals to the p_z suborbital. The p_x and p_y occupations decrease from 0.176 and 0.187 to 0.174 and 0.185, respectively, while the p_z occupation grows from 0.204 to 0.208. The principal component of the electric field gradient, the direction of which is indicated by the arrow in Fig. 2(f), grows from 4.2×10^{21} to 5.3×10^{21} V/m², whereas the asymmetry parameter decreases from 0.207 to 0.153. The experimental value is 5.5×10^{21} V/m² with an asymmetry parameter of 0.179.²⁹ The finite U_{eff} of the $4p$ electrons is related to the anomalous spatial contraction of the valence orbitals in α -Ga, which is a consequence of the incomplete screening of the nuclei by a relatively shallow Ga $3d$ state.³⁰ For the same reason, also a localization of the $4s$ electrons would be expected. Unlike the $4p$ electrons,

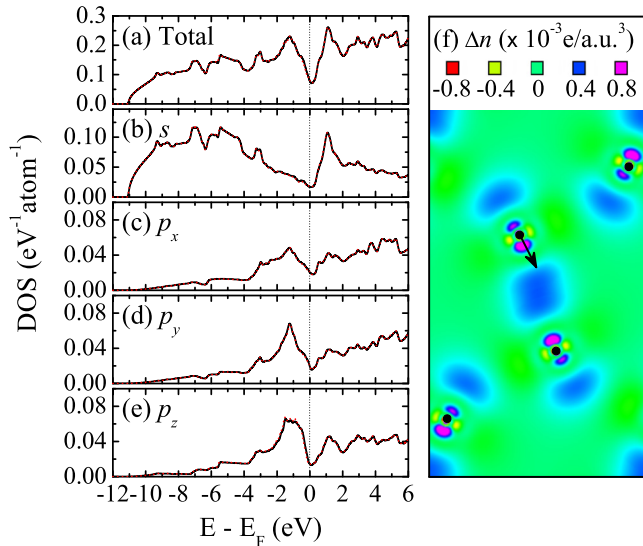


FIG. 2. (Color online) [(a)–(e)] Total and partial DOS obtained for the GGA-WC (solid curves) and extended AMF (dotted curves) methods. (f) Charge density difference Δn in the (100) plane at $x=0.5$. The positions of the Ga atoms are indicated by dotted vertical lines.

however, the U_{eff} has no effect on the $4s$ electrons in the AMF approximation.²

By Eq. (1), a symmetry lowering due to electronic correlations is to be expected. Because an asymmetric crystal structure will result in asymmetric orbital populations, $p_{\text{asymm}} = \{\sum_{m,\sigma} [(n_{m,\sigma} - \bar{n}_{\sigma}) / \bar{n}_{\sigma}]^2\}^{1/2}$, the electronic correlation energy is related to the asymmetry of the structure by the relation $E^{\text{AMF}} = -U_{\text{eff}} \bar{n}^2 p_{\text{asymm}}^2 / 2$, where $\bar{n} = \bar{n}_{\uparrow} = \bar{n}_{\downarrow}$ in non-magnetic α -Ga. Electronic correlations thus stabilize a crystal structure with lower symmetry, due to a smaller E^{AMF} . This picture is confirmed by the successful prediction of the quadrupolar lattice distortion in the perovskite compound KCuF_3 ,³ where the introduction of the U parameter creates a “mexican-hat” shaped energy surface. This shifts the energy minimum toward a lattice with lower symmetry. The symmetry lowering due to electronic correlations is also reflected by the orbital polarization of the extended AMF potential functional in Eq. (2). If $n_{m,\sigma}$ is larger (smaller) than \bar{n}_{σ} , it further increases (decreases) due to a smaller (larger) $V_{m,\sigma}^{\text{AMF,mt}}$. The orbital polarization manifests in the aforementioned occupation numbers of α -Ga.

If electronic correlations are present in α -Ga, the symmetry effect should be seen in the Ga phase diagram. The Ga-IV phase, which has a face-centered cubic structure, occurs only at pressure >120 GPa.³¹ In contrast, the α -Ga phase, which has an orthorhombic structure with the lowest symmetry, is the most stable phase at ambient conditions.^{15,16} For quantitative description, we use the pressure at which a phase occurs as measure of its stability, i.e., higher/lower pressure corresponds to lower/higher stability. In Fig. 3 we show p_{asymm} as a function of pressure. The results confirm that structures with lower symmetry give rise to more stable phases.

In conclusion, we have extended the AMF functional to describe correlation effects of less localized p electrons. The partial covalency of α -Ga, which is underestimated in LDA/GGA calculations, is improved by our approach. This shows that finite electronic correlations are present in the partially

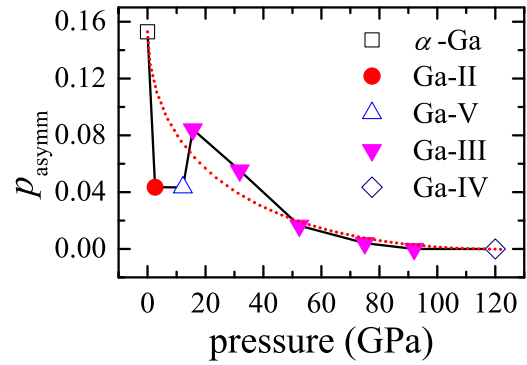


FIG. 3. (Color online) Relation between asymmetry, characterized by p_{asymm} , and stability, characterized by the pressure at which a phase occurs, for various Ga crystalline phases. The data are taken from Refs. 15, 16, 31, and 32. The dotted line is a guide to the eye.

filled $4p$ orbitals. They are reflected by the crystal symmetry of the different phases in the Ga phase diagram.

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