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First-Principles Study of Structural and Electronic Properties of UGa_3

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Abstract: In this paper, the structural and electronic properties of UGa_3 have been investigated using the generalized gradient approximation (GGA) in the presence and in the absence of spin-orbit coupling (SOC) within the density functional theory (DFT). The calculated structural parameters and electronic specific heat coefficient are in better agreement with experiment compare to other results. The electronic density of states (DOS) of UGa_3 shows that the effect of spin-orbit coupling is significant and cause to remove the spin degeneracy and split 5f partial DOS of U. Also, the partial DOS shows that there is a hybridization between U 5f and Ga 4p orbitals in UGa_3. The calculated electric field gradient as a function of unit cell volume shows that the EFG increase with pressure. Furthermore, we found that SOC increases the electronic specific heat coefficient and the electric field gradient.

Key words: Density functional theory (DFT) · Electric field gradient (EFG) · Spin-orbit coupling · Uga_3 · WIEN2K

INTRODUCTION

The UGa_3 crystal has a cubic structure of the Cu_3Au type that forms antiferromagnetically at T_N=67 K with a propagation vector q=(1/2,1/2,1/2) [1]. The antiferromagnetic structure in UGa_3 is rather simple, the uranium moments couple ferromagnetically in the (111) planes and each such plane couples antiferromagnetically to the two neighboring (111) planes. Some of distinctive properties are a ordered moment of 0.75 μ_B/U or 0.95 μ_B/U, a relatively large γ= 50mJ.K^{-2}.mol^{-1} value and a strongly reduced magnetic entropy of 0.14Rln 2 at T_N [2-5]. UGa_3 is a metal with equal carrier numbers of electrons and holes. In the de Haas-van Alphen experiments detected cyclotron effective mass is relatively large, ranging from 2.3 to 9.4m_0 [6]. During the last two decades, a few theoretical and experimental calculations have been performed to investigate properties of UGa_3. The enthalpy and the Gibbs free energies of formation of UGa_3 was measured by different calorimetric methods [7,8] and molten salt galvanic cell measurements [9,10], respectively. Kaczorowski *et al*., studied UGa_3 by means of electrical resistivity, magnetic susceptibility, specific heat and thermal conductivity measurements [2,3,11]. Their results suggest an itinerant-electron nature for the magnetism of UGa_3. The ordered magnetic moment was determined by a neutron diffraction measurement, which gives, 0.7 μ_B/U at 5K [12]. There are few experimental reports on the Fermi surface properties [9], although the energy band and the electronic structure of UGa_3 have been calculated by several authors on the basis of local spin density-functional theory [13-16]. Magnetic resonant x-ray scattering (MRXS) at the K edge of Ga in an antiferromagnetic phase of UGa_3 has been studied on the basis of a band structure calculation [17]. The optical properties of the intermetallic compound UGa_3 have been determined by means of ellipsometric measurements [18]. High pressure transport study revealed non-Fermi-liquid behavior around the critical pressure P_c = 2.6 GPa [19]. Pressure effect on magnetic properties of UX_3 (X=Al, Ga, In, Si, Ge) compounds was calculated [20]. A theoretical analysis of positron annihilation studies of two isostructural f-electron compounds $CeIn_3$ and UGa_3 was performed [21]. Kathirvel *et al.,* investigated Correlation between high pressure structure stability and electronic structure of UGa_3 up to 30 GPa [22].

To the best of our knowledge there are no theoretical calculations based on the full potential linearized augmented plane wave (FP-LAPW) method with generalized gradient approximation (GGA) [23]. Therefore,

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the aim of this paper is investigation the structural, electronic properties of UGa_3 using (FP-LAPW) method by WIEN2K [24] package. The calculations are based on the density functional theory (DFT) using the generalized gradient approximation (GGA) and local density approximation (LDA) [25] in the presence and in the absence of spin-orbit coupling (SOC).

Also, to our knowledge there is no report on the electric field gradient (EFG) of UGa_3. During the analysis of the results, special attention is devoted to the questions that so far could not be answered by the experiments: (i) What is the effect of spin-orbit coupling on structural and electronic properties? (ii) What is the effect of spin-orbit coupling on EFG? (iii) Which electrons contribute most to the EFG at Ga sites? (vi) What is the effect of pressure on EFG?

The present work is organized as follows: the details of calculation are given in next section, then results are discussed and finally, the conclusion is given.

Method of Calculation: The first-principles calculations are based on density functional theory (DFT). The total energies are calculated within the full potential linearized augmented plane wave (FP-LAPW) method, by WIEN2k package [24]. The UGa_3 crystal has a cubic structure with space group pm3m and the lattice constant of 4.248 Å [21]. The cutoff energy, which defines the separation between the core and the valence states, was set to-7.5 Ry. The muffin-tin radius was taken as 2.7 a.u. for U and 2.4 a.u. for other element. The maximum angular momentum quantum number as a cutoff for expanding the Kohn-Sham wave functions in terms of lattice harmonics inside the muffin-tin spheres was confined to L_{max} = 10. The convergence parameter RK_{max}, which controls the size of the basis sets in these calculations, was set to 7. The charge density and the potential were Fourier expanded in the interstitial region up to G_{max}=16 $(Ry)^{1/2}$.

Self-consistency is obtained by 120 special k points in the irreducible wedge of the Brillouin zone.

RESULT AND DISCUSSION

Structural Properties: We have used the experimental lattice parameter [21] as the starting point and fitted the results with a Murnaghan equation of state [26]. This procedure is carried out in the presence and absence of spin-orbit coupling (SOC) and spinpolarized. Fig. 1 indicates the total energy versus volume in above mentioned approaches. In Table 1 we have summarized our results and compared them with the experimental data and the available theoretical results. We have found that the calculated equilibrium lattice parameters in GGA+SOC are in better agreement with the available experimental values compared to GGA. The inclusion of SOC reduces the total energy and thus improves lattice constant. In addition, the calculated bulk modulus in GGA is in better agreement with the experimental value [27] compared to LDA approximation. In the following, we have calculated the pressure derivative of bulk modulus (B'). It is seem that spin-orbit coupling (SOC) and spinpolarized have considerable affects on the results and must be considered for heavy fermion compounds.

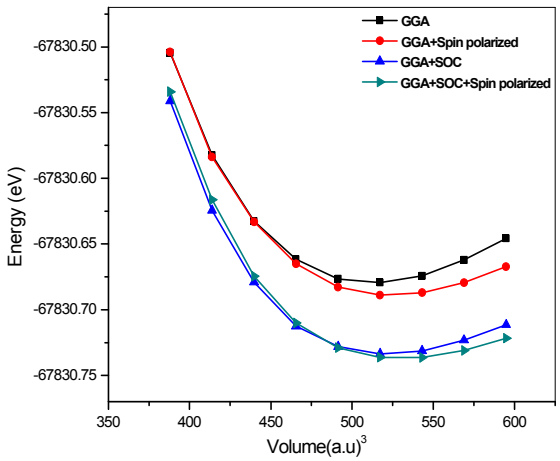

Fig. 1: Calculated total energies as a function of volume for UGa_3 in GGA, GGA+spinpolarized, GGA+SOC and GGA+SOC+spinpolarized.

Table 1 Calculated equilibrium lattice parameter, bulk modulus and its pressure derivation for UGa_3

	a(Å)	B(GPa)	B'
GGA	4.235	99.24	4.40
GGA+Spinpolarized	4.266	84.74	4.54
SOC+GGA	4.259	86.40	5.05
LDA	4.137	118.56	4.70
LDA+SOC	4.154	109.32	5.60
GGA+SOC+ Spinpolarized	4.284	81.92	4.70
Exp.	4.248[21]	99[27]	-
Theor.	4.073[15]	110[15]	-

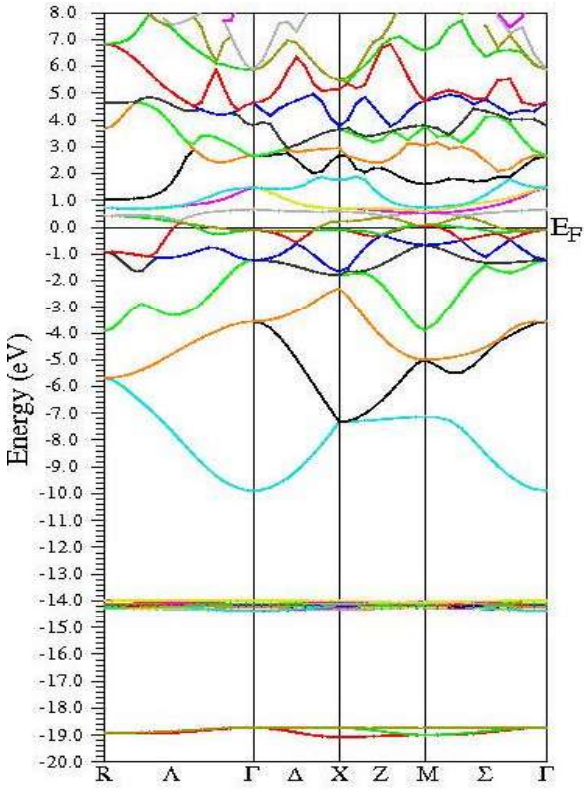

Fig. 2: The band structure of UGa_3 with GGA.

Electronic Structure: Investigation of energy bands structure is suitable way for identification of many properties of materials. The calculated electronic band structures of UGa_3 along the various high symmetry lines are given in Fig. 2. The Fermi level is set at zero. The valence and conduction bands overlap considerably and there is no band gap at the Fermi level. This finding confirms the metallic nature of this compound [15]. The width of valance band is from-10 eV to 0 eV that relevant to different orbitals participation. In lower part of the valence band, the Ga d and the U p orbitals are located at-14 eV and-19 eV, respectively.

Our calculated total density of states (DOS) for UGa_3 is given in Fig. 3(a). The overall DOS spectrum are in good agreement with the previous theoretical results [13, 15, 17]. There is no band gap for this material andthe DOS has a large finite value at the Fermi level. Once again, this finding indicates the metallic nature of UGa_3 and confirms band structure. Total density of states is given with spinpolarized in Fig. 3(b). Small difference is seen in Fig. 3(b) between the DOS for m= +1 and m=-1 states from approximately-2.5 eV to 2.5 eV and this difference becomes the largest from 0 eV to 2 eV. The difference between up DOS and down DOS signify on existence of magnetic properties in this compound.

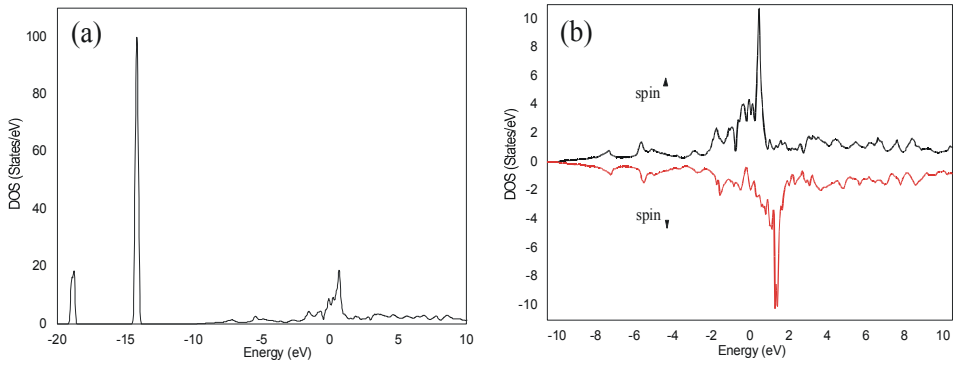

Fig. 3: The total density of states (a) with GGA and (b) GGA + Spin polarized. The vertical dashed line indicates the Fermi level.

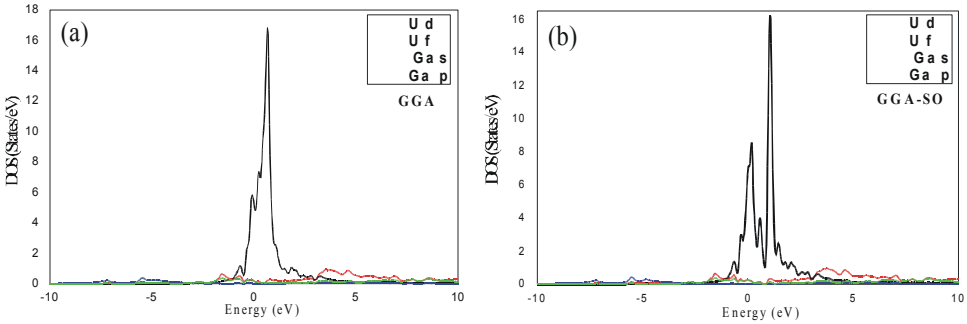

Fig. 4: Partial DOS of UGa3 (a) with GGA and (b) GGA + SOC. The vertical dashed line indicates the Fermi level.

Table 2: The electronic specific heat coefficient and λ of UGa_3

	GGA	GGA+SOC	LDA	LDA+SOC	Theor.	Exp.
λ(mJ/mol*K^2)	18.05	28.05	17.81	30.24	21.9[6]	50[2]
λ	1.77	0.78	1.81	0.65	1.55	-

Table 3: Main component of EFG tensor at Ga sites and different contributions to the electric field gradient. V_{zz} is given in the units of 10^{21} V/m^2

	V_{zz}	Valence contr.	p-p	s-d	d-d	p-f	f-f
GGA	9.91231	9.92005	10.39017	0.02195	-0.52615	0.02602	0.00031
GGA-SO	10.04633	10.046446	10.53753	0.02256	-0.53998	0.0259	0.00032

In order to investigation quality of participation of different orbitals we have calculated partial DOS for UGa_3 in the presence and absence of spin-orbit coupling in Fig. 4. It is clear that all orbitals participate in bonding formation and there is hybridization between gallium 4p states and uranium 5f states which leads to a narrow band of itinerant 5f states.

According to Fig. 4 uranium 5f states DOS at the Fermi level are major than others. Spin-orbit coupling cause to remove the spin degeneracy and so 5f partial DOS of U split into two parts. These two peaks correspond to the j=5/2 and j=7/2 5f sub-bands. The peak corresponding to j=5/2 is nearly filled. Using the calculated DOS at the Fermi level, we have calculated the electronic specific heat coefficient γ defined as [28]

$$\gamma = \frac{\pi^2}{3} k_\beta^{\,2}\, g(\varepsilon_F)$$

where k_β is the Boltzman constant and $g(\varepsilon_F)$ is the DOS at the Fermi energy. The results are given in Table 2 within GGA and LDA approaches with and without spin-orbit coupling. The inclusion of SOC increase DOS at Fermi level that improves γ. The calculated electronic specific heat coefficient with LDA+SOC is closer to experimental value [2] in comparing to other theoretical results [6]. The connection between the calculated and experimental values of γ is usually written as [29].

$$\gamma_{\exp} = \gamma_{band}(1+\lambda)$$

where λ is an enhancement factor taking electron-phonon interaction and many other body effects into account. The results are given in Table 2.

Electric Field Gradient: The electric field gradient a traceless symmetric tensor of rank 2 and proportional to the deviation of electron distribution in the vicinity of the nucleus from a spherical distribution. The principal component of EFG which is V_{zz} can be obtained directly from the charge density in the following way [30].

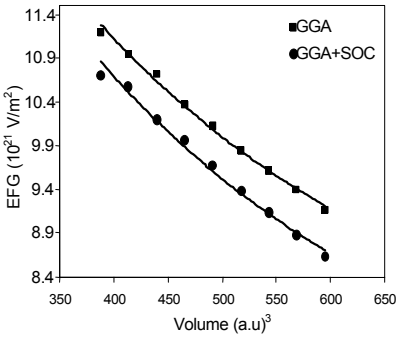

Fig. 5: The effect of pressure on the EFG at Ga site in UGa_3.

$$V_{zz} = \int \rho(r) \frac{2P_2(\cos\theta)}{r^3} dV$$

Where P_2 is the second order Legendre polynomial. Inside the atomic sphere, the electron density distribution is described by the formula

$$\rho_{LM}(r) = \sum_{E\langle E_F} R_{lm}(r) \sum_{l,m} R_{l'm'}(r) \sum_{l'm'} G_{LM}^{Mmm'}$$

Where R_{lm} are the radial functions with the angular momentum l or l and $G_{LM}^{Mmm'}$ are the Gaunt coefficients. Since the polynomial P_2 is proportional to Y_{20}, only the quantity $\rho_{20}(\vec{r})$ should be taken into account. The Gaunt numbers also impose constraints on the possible contributions to the electron density. for L = 2 and M = 0, only $l = l' = 1$ and $l = l' = 2$ give nonzero Gaunt coefficients ($l = 0, l' = 2, l = l, l' = 3$ and $l = l' = 3$ give laser measure). Hereafter, we have used the generally notation for these contributions: p-p and d-d (s-d, p-f, f-f), respectively. The Ga nucleus in UGa_3 having a non cubic symmetry, exhibit the electric quadrupole interaction and have nonzero EFG. Main component of EFG tensor at Ga sites and decomposition of the valence contribution in the presence and absence of spin-orbit coupling (SOC) are given in Table 3. This table indicates that the dominant contribution to EFG comes from electrons with p-character. We have calculated the effect of pressure on the EFG at Ga site in UGa_3 with and without spin-orbit coupling in Fig. 5. When pressure is imposed,

the electronic shells loss their symmetry and because the anisotropy parameter is being large, the EFG increases with the pressure. Also, The SOC increases the value of EFG and shifts the calculated EFG down by a marginal value that is rather independent of the unit cell volume.

CONCLUSIONS

In this study, we have presented a theoretical analysis of the structural and electronic properties of UGa_3 by using FP-LAPW method. The equilibrium lattice parameter calculated with GGA approximation in the presence of SOC and the bulk modulus value in the absence of SOC are in better agreement with the experiment. The derivative of bulk modulus is not available for UGa_3 and this is the first report on the theoretical value of B' for this compound. The calculation of electronic structure showed that UGa_3 is a metallic compound and there is hybridization between gallium 4p states and uranium 5f states which leads to a narrow band of itinerant 5f states. The calculated electronic specific heat coefficient in the presence of SOC is in better agreement with the experimental value comparing others. The experimental electric field gradient value is not available for UGa_3 and this is the first report on the theoretical value of EFG for this compound. Also, the effect of pressure on EFG for this compound was investigated and it was found that its value increases with pressure. Calculations showed that SOC increases the value of EFG and shifts the calculated EFG down.

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