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# Cancellation of spin and orbital magnetic moments in δ-Pu: theory

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**ABSTRACT**

Density functional theory (DFT), in conjunction with the fixed-spin-moment (FSM) method, spin-orbit coupling (SO), and orbital polarization (OP), is shown to retain key features of the conventional DFT treatment of δ-Pu while at the same time not producing the substantial net magnetic moments commonly predicted by this theory. It is shown that when a small adjustment of the spin moment (less than 20%) is allowed, a complete spin- and orbital-moment cancellation occurs which results in a zero net magnetic moment in δ-Pu. This minor modification, accomplished by the FSM method, is shown to have a very small effect on the calculated total energy as well as the electron density-of-states (DOS). The photoemission spectra (PES), obtained from the DOS of the present model, compares equal or better to measured spectra, than that of two other recent non-magnetic models for δ-Pu.

*Keywords*: δ-Pu; Electronic structure, Density functional theory

## Introduction

The last few years have seen an increased focus in trying to understand the actinide metals in general and plutonium in particular [1]. One of the more fundamental issues with plutonium is the existence of a highly complex ambient-pressure phase diagram with six well-defined phases (α, β, γ, δ, δ', and ε) that vary greatly in their atomic geometry and density. This provides an

extraordinary challenge for theoretical modelling and several approaches have been presented, for example the mixed-level-model (MLM) [2], the around-mean-field dynamical mean-field theory (AMF-DMFT) [3], and spin/orbital polarized DFT [4]. The two former strictly deals with the δ phase whereas the latter is able to treat the remaining phases as well.

Recently [4], calculations founded on the spin and orbital polarized DFT model were able to describe total energies, atomic densities, and bulk moduli remarkably well for all the Pu phases, with perhaps a somewhat high total energy for the melting phase. This is clear from the total energies in Fig. 1. The effects of localization (weakening of the metallic bond strengths) of the 5*f* electrons proceeding from δ to ε and so on are apparently accurately modelled by the formation of magnetic moments [4] which are smallest for the δ phase and largest for the ε phase. It was shown [4] that these moments vary in a continuous fashion universally for all phases and Pu-atom geometries, which indicates that the electronic structure is a function of the local geometry surrounding the Pu atoms. This in turn suggests that *ad hoc* approaches, distinguishing the various phases by distinct treatments, are unnecessary and probably misleading.

Although details of the theoretical electronic structure seem appropriate [5] when compared to photoemission spectra, the validity of the substantial magnetic moments in Pu has been questioned for some time and a summary can be found in Ref. 6. The lack of convincing experimental evidence of magnetic moments, contrasted by the firm DFT prediction of magnetism, pose an interesting problem in Pu. The literature offers several plausible explanations for this, for instance: (a) The magnetic moments in the DFT have no physical meaning but provide additional degrees of freedom and variational flexibility such that other electron-correlation effects are mimicked [7]. (b) Fluctuations wash out the net magnetic moments on a time scale shorter than experiments [8]. (c) Local magnetic moments are subject to Kondo screening [9]. (d) The spin moments are cancelled by anti-parallel orbital moments on each atomic site [4]. The explanations (a) - (c) cannot be investigated by a DFT approach because they rely upon deficiencies within the theory itself. The (d) explanation was proposed [4], but has not been investigated in detail.

The present report analyzes the possibility of a cancellation of the spin and orbital moments as a plausible reason for the lack of credible experimental evidence of sizeable net magnetic

moments in Pu. This is done by means of constrained DFT calculations utilizing the so-called fixed-spin-moment method [10]. The focus will be on the δ phase because of the simplicity of the cubic crystal structure and the greater magnitude of the DFT magnetic moments in this phase.

**Computational details**

The electronic-structure calculations are performed within the framework of DFT. Since the magnetic moments are the fundamental properties of interest here, and we are only considering the close-packed face-centred cubic (fcc) geometry, we have employed the linear muffin-tin orbitals method, within the atomic sphere approximation (LMTO-ASA) [11]. This technique has the advantage that both spin and orbital moments can be computed on an equal footing throughout the entire crystal, whereas in calculations not relying on the ASA, this has not been possible. The ASA has well-known challenges with accuracy of structural energies for open phases, but is robust for fcc geometries. For accurate total energies of more complex phases, i.e., α-Pu, a full-potential version of the LMTO method [12] is appropriate and was used in Ref. 4.

Our LMTO-ASA calculations are performed at the experimental lattice constant of δ-Pu, utilizing *s*, *p*, *d*, and *f* partial wave functions. Spin polarization, spin-orbit coupling, and orbital polarization are included in the conventional ways [13]. The number of **k** points in the irreducible part of the Brillouin zone ($1/16^{th}$) is about 4000 and the number of energy points for the calculation of the DOS is 8000 in a 0.7 Ry energy window. The PES is obtained from the DOS by applying instrumental and lifetime broadening as described by Arko *et al.* [14].

We only consider a ferromagnetic configuration, as it is necessary for the application of the FSM method, although it has been argued [5] that a paramagnetic state with disordered moments is a more realistic DFT model for δ-Pu. The magnitudes of both the spin and orbital moments, however, depend only weakly on the specific magnetic configuration [5]. The FSM method [10] allows for a calculation where the spin moment is fixed to any value from zero to the number of valence electrons and adds a constraint to the DFT treatment with an associated increase in the total energy. In practice, this constraint is accomplished by introducing two separate Fermi levels for each spin valence band. These could then be chosen so that the difference between spin up and down occupation results in the preferred spin moment.

A small modification of the spin moment is motivated by the fact that every DFT calculation is associated with errors arising from necessary approximations applied in the theory. One fundamental simplification is the treatment of the electron exchange and correlation interactions. Depending on the exact formulation of this approximation, the atomic equilibrium volume for a wide range of transition and actinide metals generally has an error of about 2-3%, the bulk modulus ~10-20%, and the spin moment in magnetic systems ~10-20%. The effects of an error in the spin moment can conveniently be analyzed within the FSM approach for any ferromagnetic system.

**Results**

Figure 1 shows the calculated total energy (left y-axis in red) and total magnetic moment (right y-axis in blue) as functions of spin moment for δ-Pu. Notice that the total-energy minimum occurs for a spin moment close to 3.4 $\mu_B$, which corresponds to an unrestricted calculation. The total magnetic moment is about 0.4 $\mu_B$ and the orbital moment about -3.0 $\mu_B$. These compare relatively well, but are somewhat smaller than the full-potential results [4], and suggest a near cancellation between spin and orbital magnetic moments. For spin moments smaller than about 3.4 $\mu_B$ the total moments are always very close to zero, see Fig. 1. Also, for a spin moment of about 2.8 $\mu_B$ (less than 20% decrease from the unconstrained value) the total moment is exactly zero, while the total energy has only increased by ~ 1 mRy. This small energy increase is actually close to the total-energy error of a typical DFT calculation. The less than 20% correction is still within an expected error-range for a DFT spin moment, as already mentioned.

It is clear from Fig. 1, that a zero magnetic-moment situation in δ-Pu is very easily accomplished with only a minor correction of the spin moment and the total energy. As showed in Ref. 4, the spin moments depend on atomic density and geometry, and gradually decrease when progressing through the lower temperature phases of Pu: δ, ε, and finally α. As the spin moments decreases, so do the orbital and total moments, see Fig. 1. This fact is more evident in Fig. 2, where we plot the orbital moment as a function of spin moment together with the exact cancellation ($\mu_o = -\mu_s$). For any spin moment less than about 3 $\mu_B$, the cancellation is almost complete. Notice, however, that this is true only for the computations that include orbital

polarization (blue). When OP, the generalization of Hund's second rule for an atom, is neglected and only the first (maximize spin) and third (spin-orbit coupling) rules are considered (SO: red), there is no chance for a cancellation.

We have discussed the spin dependence of the orbital moment, total moment, and total energy. The spin moment has, of course, also a fundamental influence on the electronic structure through the shifts of the respective spin up and down bands. In Fig. 3 we plot the photoemission spectra, as obtained from the theoretical DOS, for three calculations of fixed spin moment, and one unconstrained. For $\mu_s = 0$ (green: non-magnetic calculation), the PES has a broad feature that extends well below the Fermi level at zero binding energy. Already with a small spin moment of 1 $\mu_B$, this feature sharpens towards the Fermi level (purple). Finally, for $\mu_s = 2$ (red), 2.8 (blue: zero total moment), and 3.4 (black: unconstrained), the PES look relatively similar with a very sharp peak at the Fermi level and then a second broader and shallower feature which is centred at about -0.5 eV. This behaviour resembles very well the measured spectra, as we shall see below.

Next, we focus on the effects of spin-orbit coupling and orbital polarization on the calculated DOS and the corresponding PES. In Fig. 4 we show the PES from unconstrained calculations within a scalar-relativistic treatment, SR (blue: spin-orbit coupling neglected), SO (red), OP (black), together with experimental data points from a spectra by Tobin *et al*. [15]. Notice that only the OP treatment is able to reproduce the key features of the measured spectra. Clearly, the enhanced orbital moments and the associated shifts of the orbitals with spin, orbital, and magnetic ($s$, $l$, $m_l$) quantum numbers obtained from the OP scheme is important for the qualitative description of the electronic structure.

It is worth comparing the present zero-moment model with other non-magnetic approaches proposed for $\delta$-Pu. First, the MLM was developed by Eriksson *et al*. [2] and predicts a division of the 5*f* manifold into a localized part with 4 electrons and an itinerant part with the remaining 5*f* electron. Although these states hybridize, the loss of bonding associated with this "partial localization" results in a good lattice constant, mechanical stability, and a reasonable PES. The very recent AMF-DMFT model [3] is very different from both the MLM and any variation of DFT, because it assumes a $5f^6$, americium-like, electronic configuration. This assumption has several problems in itself as analyzed by Tobin *et al.* [15], which we will not discuss in detail

here. The $5f^6$ electronic configuration implies a complete occupation of the $5f_{5/2}$ band which cannot sustain any magnetic moment as it corresponds to a J=0 configuration in the atomic limit. The AMF-DMFT approach requires on-shell Coulomb interaction parameters (U ~ 3-4 eV and J ~ 0.7 eV), which are chosen to give a non-magnetic ground state while simultaneously reproduce the experimental lattice constant and bulk modulus for δ-Pu. Hence, for this model, the principal (unfitted) result is the electronic structure.

In Fig. 5, we contrast PES from two completely independent measurements [14,15] with the three theoretical models we have discussed. The two experimental data sets compare rather well, with a narrow peak, about 0.1 eV wide, at the Fermi level, with a second feature centred at about -0.5 eV. The present DFT model (red) appears to be accurately describing the average of the two measurements. The MLM model (blue) compares rather favourably as well, as has been pointed out in the literature [16]. The AMF-DMFT model, however, does not compare well with any of the experimental data points except below binding energies of about -0.75 eV.

**Discussion**

We have presented a model for plutonium, founded on conventional DFT, which incorporates a minor adjustment of the spin moment so that the total magnetic moment equals zero. Although the magnetic interactions, including orbital polarization, are important, the model is non-magnetic with respect to the total magnetic moment at each Pu site. We have shown that the minor spin-moment correction, accomplished by the FSM method, has a negligible impact on the total energy and electronic DOS. This is important because previous DFT calculations have proven that the total energy and DOS are very well described for plutonium. The electronic structure of the present model has been compared to experimental data and two alternative non-magnetic models. The inclusion of Hund's second rule, by means of orbital polarization, is important for a detailed description of the electronic structure within the DFT, while the MLM also appears to reasonably well reproduce the measured spectra. The electronic structure of the AMF-DMFT, however, neither reaches the level of precision of the present DFT nor the MLM. This is a problem because the electronic structure is the fundamental output for which this model can be validated by experiment.

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**Figure captions**

1. DFT total energies for plutonium. Reproduced from Ref. 4.
2. Calculated total energy (left y-axis in red) and total magnetic moment (right y-axis in blue) as functions of spin moment. An expected DFT error in the spin moments is bracketed with vertical dashed lines.
3. Calculated orbital moment with (OP) and without (SO) orbital polarization, as functions of spin moment. The green line symbolizes the exact spin- and orbital-moment cancellation.
4. Calculated PES for spin moments fixed to 0 $\mu_B$ (green), 1 $\mu_B$ (purple), 2 $\mu_B$ (red), and 2.8 $\mu_B$ (blue). The black line shows an unconstrained calculation where the spin moment is about 3.4 $\mu_B$. The blue curve shows a calculation with complete spin- and orbital-moment cancellation.
5. Calculated PES without spin-orbit interaction (SR: blue), with spin-orbit interaction (SO: red), and with orbital polarization (OP: black), together with experimental data points by Tobin *et al*. [15].
6. PES as obtained from three non-magnetic models, the present DFT with zero total moment due to spin- and orbital-moment cancellation (red), the MLM [2] (blue), and the AMF-DMFT [3] (green). Experimental data are from Arko *et al.* [14] (open squares) and Tobin *et al.* [15] (filled circles).

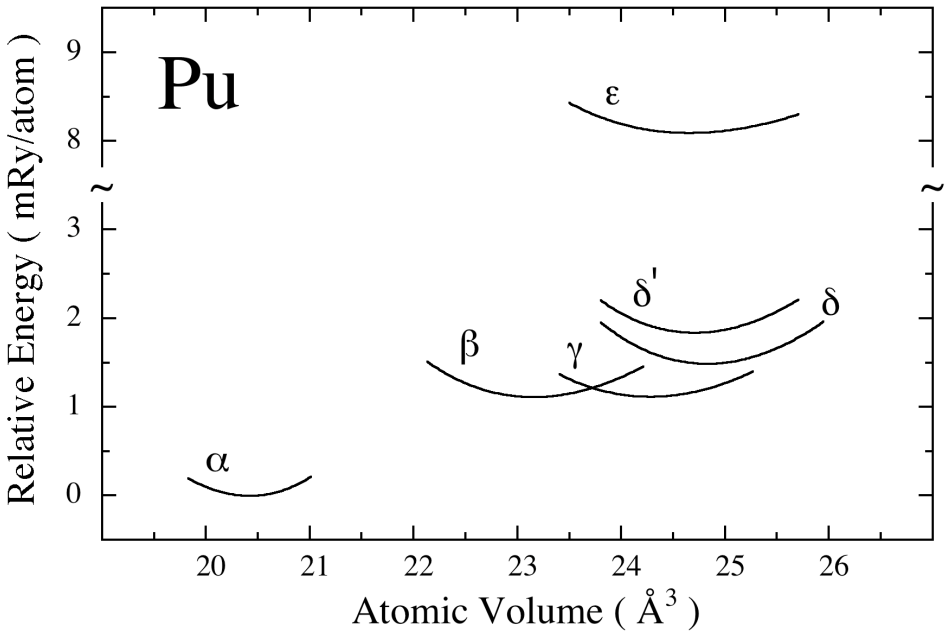
Pu
ε
δ'
δ
β
γ
α
Relative Energy ( mRy/atom )
Atomic Volume ( Å$^3$ )
9
8
3
2
1
0
20
21
22
23
24
25
26

**Figure 1.**

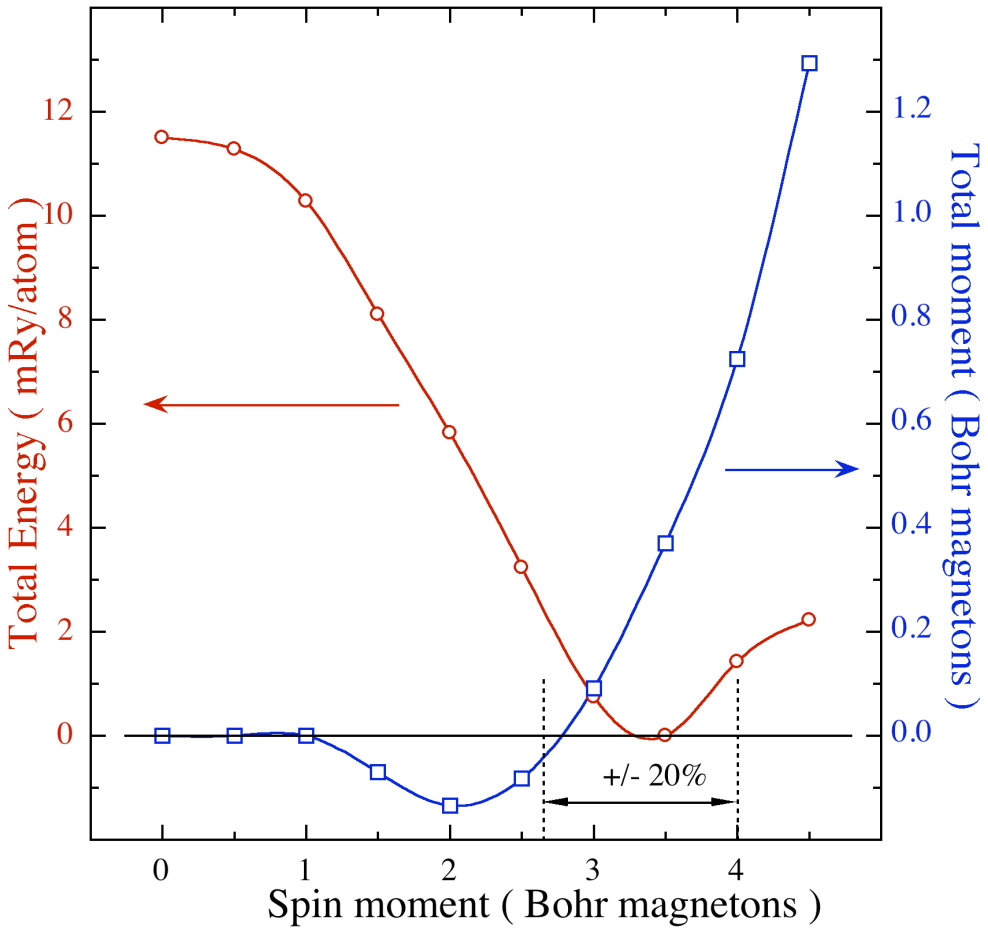
Total Energy ( mRy/atom )
Total moment ( Bohr magnetons )
Spin moment ( Bohr magnetons )
+/- 20%
0
2
4
6
8
10
12
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
1
2
3
4

**Figure 2.**

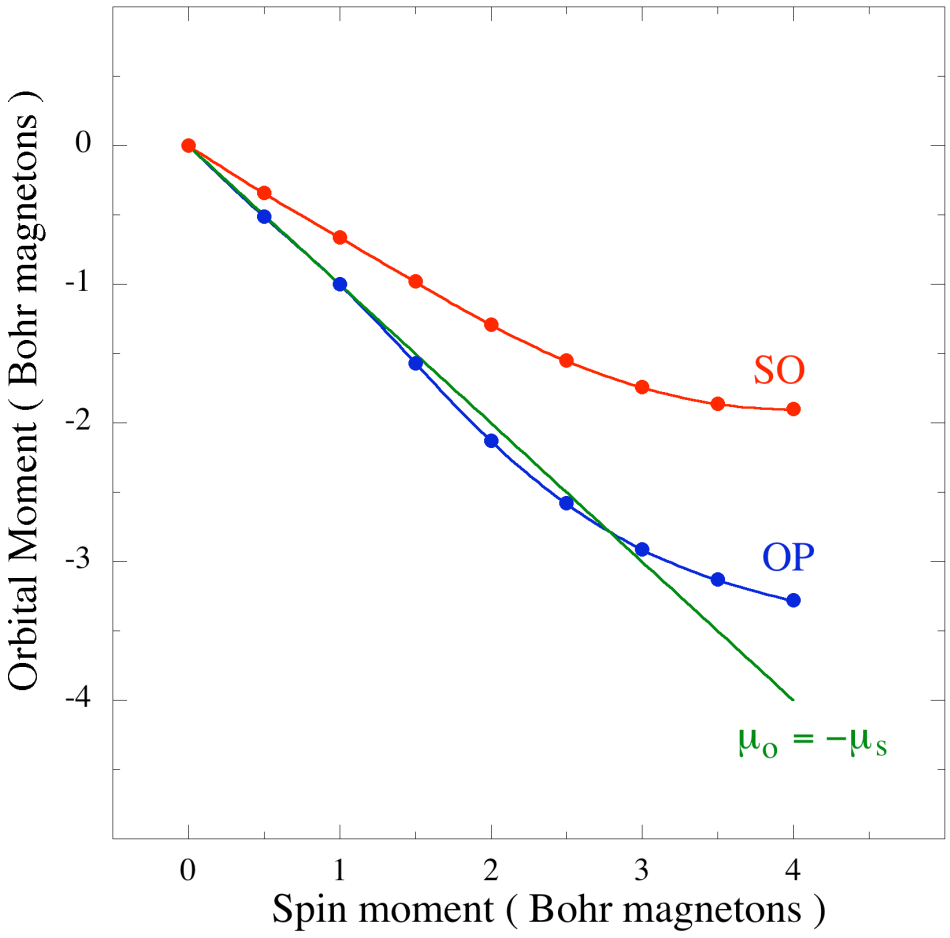
Orbital Moment ( Bohr magnetons )
0
-1
-2
-3
-4
SO
OP
$\mu_o = -\mu_s$
0
1
2
3
4
Spin moment ( Bohr magnetons )

**Figure 3.**

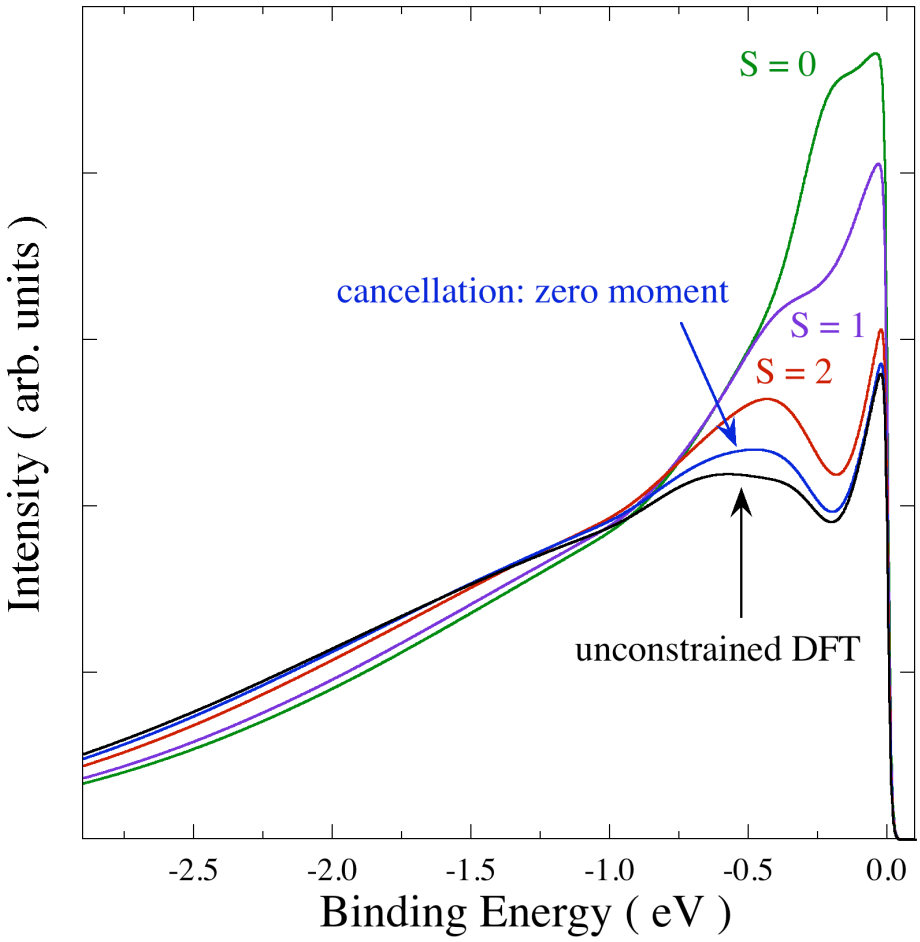
S = 0
cancellation: zero moment
S = 1
S = 2
unconstrained DFT
Intensity ( arb. units )
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
Binding Energy ( eV )

**Figure 4.**

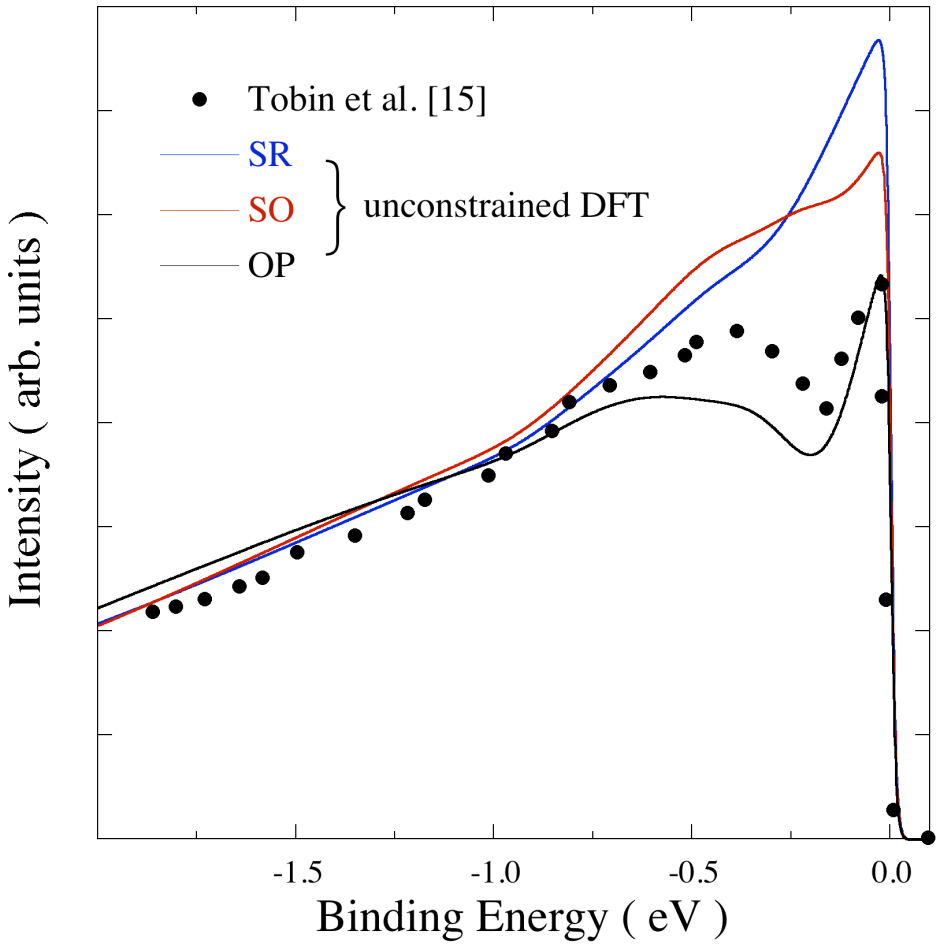
Tobin et al. [15]
SR
SO
OP
unconstrained DFT
Intensity ( arb. units )
-1.5
-1.0
-0.5
0.0
Binding Energy ( eV )

**Figure 5.**

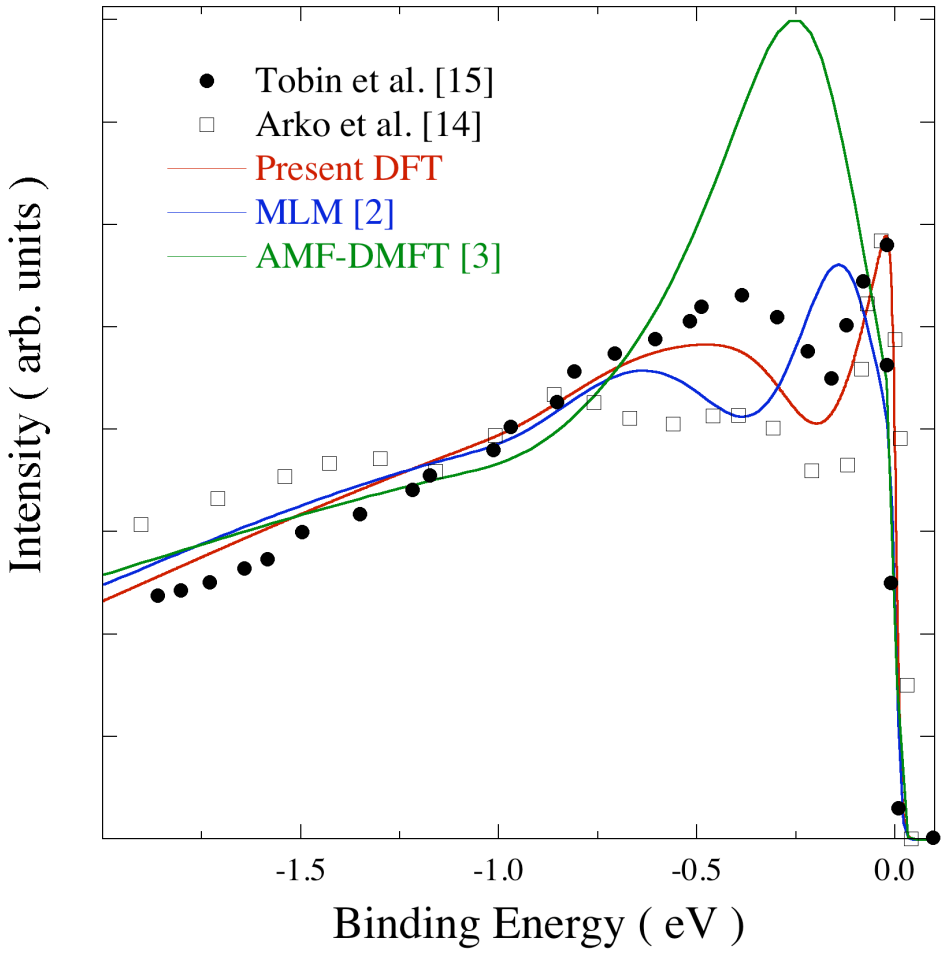
Tobin et al. [15]
Arko et al. [14]
Present DFT
MLM [2]
AMF-DMFT [3]
Intensity ( arb. units )
-1.5
-1.0
-0.5
0.0
Binding Energy ( eV )

**Figure 6.**