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Field-induced magnetization of δ -plutonium from density-functional theory

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Abstract

We present results from density-functional theory (DFT) calculations of magnetization, induced by an external magnetic field, for δ -phase plutonium. The fully relativistic electronic structure accounts for Zeeman splitting effects through a Hamiltonian that couples the magnetic field to both spin and orbital magnetic moments. The electronic-structure model is further improved by an extension to DFT in terms of an orbital-orbital coupling via the conventional orbital-polarization method as has routinely been done for plutonium. The response to the applied magnetic field is shown to be weak in the DFT model, with induced magnetic moments of the order of $10^{-3} \mu_B$ in magnetic fields up to 30 T. These results are in accord with recent assessments from X-ray Magnetic Circular Dichroism (XMCD) measurements in magnetic field on δ plutonium. Somewhat surprisingly, a model assuming δ plutonium to be absent magnetic moments shows stronger response to an external static magnetic field than models allowing for antiferromagnetism or magnetic disorder.

I. Introduction

The electronic structure of materials is usually analyzed at ambient conditions, i.e., room temperature and atmospheric pressure. Sometimes applied pressures up to several Mbar can cause significant changes of the electronic structure and drive phase transitions due to the large excitation energies associated with such large compressions [1]. Other times, the effect of a lower energy scale temperature increase can lead to interesting electronic-structure phenomena that can drive phase transitions such as the isostructural ($\alpha - \gamma$) phase transition in cerium, see discussions in Ref. [2].

The phase diagram of plutonium is sensitive to both pressure and temperature, and at about 600 K the face-centered cubic (fcc) δ phase becomes stable [3]. At room temperature, at a much-compressed volume relative to the δ phase, the ground-state monoclinic α phase is formed. With only a few hundred degrees separating the phases, their respective energies must be comparatively close. Ab initio density-functional calculations reproduce this behavior (and the presence of other plutonium phases) rather accurately [4]. More recently, first-principles thermodynamical calculations [5, 6, 7] nicely capture the finite temperature characteristics of δ plutonium, including the anomalous Invar effect (negative or small thermal expansion), heat capacity, and Gibbs free energy.

Experimentally, calorimetric entropy measurements on the α and δ phases of plutonium were suggested to imply a very narrow 5f-band scenario [8] in plutonium driving a structural Peierls distortion [9]. The narrow bands emerge from DFT calculations [9], but also from dynamical mean-field theory (DMFT) calculations [10, 11, 12].

A more subtle way to perturb the electronic structure is by applying an external magnetic field. The energy associated with a static magnetic field with a strength achievable experimentally is on a low energy scale and the field would not likely drive any phase transitions. Nonetheless, measurements of magnetization in magnetic fields are quite widely done and provide valuable information about the electronic structure of both magnetic and nonmagnetic materials. Particularly interesting is plutonium

metal because for such a heavy element with a nearly half-full 5f shell, the relativistic spin-orbit interaction is substantial and the orbital magnetic moment, in addition to the spin moment, couples to the magnetic field. Therefore, the magnetic spin and orbital moments induced by the magnetic field may show intriguing behaviors. For example, as expected from Hund's third rule of the atoms, for less than a half full shell, the spin and orbital moments shall align antiparallel. One may wonder if this fundamental rule still holds true in the presence of an external magnetic field. This question and the recent experimental X-ray Magnetic Circular Dichroism (XMCD) studies of gallium-stabilized δ plutonium in a magnetic field [13], motivates a theoretical investigation of field-induced magnetism in δ plutonium. Although plutonium has been thoroughly investigated and modeled in various ways, this magnetic field study is the first of its kind for the δ phase.

Density-functional electronic structure calculations are commonplace for materials exposed to pressure and temperature, but far less frequent for materials in the presence of an external magnetic field. For an accurate electronic structure in this case, one must consider a coupling between the magnetic field and the spin and orbital moments [14]. These interactions give rise to the Zeeman effect that affects the electronic structure and impacts the magnetic moments, and the modified Fermi surface geometry can be observed in de Haas-van Alphen experiments. Such experiments have not been reported for plutonium metal but for the plutonium intermetallic compound PuIn_3 [15]. The Fermi-surface topology has, however, been calculated [16] for δ plutonium.

In this Letter we investigate the δ phase of plutonium in static magnetic fields up to 30 T, focusing on the net magnetization and its contribution from spin and orbital moments. For accurate magnetic moments we introduce a perturbation of the Hamiltonian that accounts for the Zeeman interactions within the context of advanced self-consistent DFT calculations. Our results compare favorably with recent experimental XMCD [13] assessments for δ plutonium. The good agreement, i.e.,

very small field induced alignment of magnetic moments in δ plutonium, contradicts the presumption that the DFT model predicts giant field induced magnetization.

Section II deals with computational details and methodology, and in Sections III and IV we present our results and conclusions.

II. Computational details and methodology

In our model for plutonium, we assume that the 5f electrons are itinerant (delocalized). The alternative is that these electrons are described as fully localized or partially localized, where in the latter, the 5f manifold is divided into parts with localized and delocalized electrons such as in the model by Eriksson et al. [17], for example. But, the hypothesis of delocalized or itinerant 5f electrons has been very productive and many plutonium properties including its complex phase diagram follow from this concept [4].

Our fundamental theoretical and technical approach is described extensively in our review article on plutonium [18] and we will not repeat all the details here. In brief, we apply an all-electron full-potential linear muffin tin orbitals (FPLMTO) methodology [19], where spin-orbit interaction and orbital polarization are included, with no need for any adjustable parameters. For δ plutonium, we allow for itinerant magnetism (spontaneous spin polarization) although ferromagnetic order, yielding a net magnetization, was immediately ruled out due to its high energy [20]. Furthermore, it was shown [21] that an entirely nonmagnetic treatment, where spin and orbital moments are constrained to zero, results in a state with an unrealistically high energy and with an indefensible (small) lattice constant. Instead, one concluded that reasonable and computationally practical models for δ plutonium include an antiferromagnetic (AF) or a disordered magnetic (DM) state [21]. The DM state seems to be more justifiable based on its mechanical stability and the fact that it is favored at δ -phase temperatures due to the magnetic disorder entropy [22]. The DM state was also argued to best represent possible dynamic

magnetic moments (spin fluctuations) that was only observed in neutron-scattering experiments much later [23]. Both the AF and the DM approaches result in excellent theoretical atomic volumes for δ plutonium ($25 \text{ \AA}^3$), but to take some of the effect of Ga into account from the real experimental 2 at. % Ga sample [13], we conduct all calculations at the measured atomic volume for this particular gallium alloy ($24.7 \text{ \AA}^3$). To ensure good magnetic moments, the number of k points used for integrations in the reciprocal space are about 200 for the largest cell but considerably more for the crystal structures with fewer atoms. To each energy eigenvalue we apply a Gaussian broadening with a 20 mRy width.

In this Letter, we apply an unconventional DFT treatment for δ plutonium. In addition to the more traditional spin-orbit coupling and orbital polarization effects on the electronic structure, the presence of a static magnetic field, $\mathbf{B}$, necessitates the Zeeman interaction that is included as a perturbation, H_Z , to the conventional Hamiltonian, where

$$H_Z = \mu_B \mathbf{B} \cdot (\mathbf{l} + 2\mathbf{s}) \quad (1)$$

The orbital, $(\mathbf{B} \cdot \mathbf{l})$, and spin, $(\mathbf{B} \cdot 2\mathbf{s})$, coupling terms are calculated self-consistently as usual with the other contributions within the complete DFT Hamiltonian. For a detailed description of the implementation of this Zeeman Hamiltonian in a self-consistent DFT method, we refer to Hjelm and Calais [14].

For the DM configuration, a standard 8-atom fcc special quasi-random structure (SQS8) [24], we calculate the magnetization due to the magnetic field up to 30 T. The result of one calculation using a larger 32-atom special quasi-random structure cell (SQS32) is used to confirm the accuracy of the smaller (SQS8) cell. For a magnetic field of 6 T, the field strength applied in the XMCD experiment [13], we also investigate the AF configuration; type I with spins aligned collinearly in $\langle 100 \rangle$ ferromagnetic sheets with adjacent sheets having antiparallel spins and the spin quantization along the $[001]$ direction.

For comparison, and to explore a notion [13] that plutonium may be completely nonmagnetic with neither spin degrees of freedom nor any unconventional magnetism, we calculate the magnetic-field response to nonmagnetic δ plutonium at 6 T as well. The nonmagnetic treatment is designed with a 1-atom fcc cell with the same computational parameters as all the other calculations. The difference is in the initial configuration that was nonmagnetic with the spin up and down states being numerically equal, i.e., a metastable state that did not spontaneously spin polarize.

III. Results

We begin considering the disordered magnetic state [21] for our calculations of the δ phase. This configuration has zero magnetization outside of a magnetic field, due to the lack of magnetic order, and is in this sense analogous to a paramagnetic or spin fluctuating state. In Figure 1, we show results from two treatments of the Zeeman effect. First, in the upper panel, the full Zeeman Hamiltonian is applied. We here include terms arising from both spin and orbital contributions. Second, in the lower panel, we exclude the orbital-moment interaction with the magnetic field leaving only the spin coupling.

In analyzing the differences between the full Zeeman theory and the model without orbital-moment coupling to the field, we first notice that both models predict small magnitudes of the magnetic moments that increase linearly with the field. This trend actually holds true well beyond 30 T (not shown). Also, for the complete Zeeman Hamiltonian (Eq. 1), the induced spin and orbital moments align parallel, while in the spin-only Hamiltonian they align antiparallel. The driving force for the antiparallel arrangement of spin and orbital moments, in a less than half full shell, comes from Hund's third rule, namely the spin-orbit coupling. On the other hand, the Zeeman orbital moment interaction with the magnetic field tends to align the spin and orbital moments parallel in the field direction. There is thus a balance between these two mechanisms that will be material dependent, but in the case of δ plutonium, the orbital moment coupling to the magnetic field dominates over the spin-orbit interaction. Hence, for

the complete Zeeman Hamiltonian (Eq. 1), we have a scenario where the spin and orbital moments are parallel. Furthermore, the magnitudes of the moments are very small, regardless of the level of approximation, and of the order of $10^{-3} \mu_B$. In a recent XMCD study [13], an upper limit of $0.1 \mu_B$ on the magnetic moment magnitudes was proposed at 6 T and our calculations predict moments that are far below this upper constraint even in the much stronger field of 30 T. There are discussions in Ref. [13] regarding how polarized or saturated δ plutonium may be at the 6 T experimental condition. In our DFT model, it is straightforward to calculate the effect of large magnetic fields and even at 600 T, there is no realignment of spins or magnetic saturation in the model. This result suggests that at the 6 T applied magnetic field in the experiment, the polarization in δ plutonium is less than 1%.

In Table 1 we also consider the antiferromagnetic and nonmagnetic configurations, now only for an applied field of 6 T with the full Zeeman Hamiltonian. Again, very small and parallel magnetic moments are induced by the field, regardless of configuration. We note that the AF configuration responds almost identically to the DM state. To validate our treatment of the DM state, we also calculate the 30 T magnetic field response for a larger (SQS32) cell and the magnetic moments decreased 10%, thus not changing any of our conclusions. The rather similar behavior of the AF and DM configurations implies that the computationally more efficient AF approach may suffice for δ plutonium. Another magnetic configuration that can be practical is the 3Q non-collinear structure proposed by Rudin [25]. But to accurately calculate induced magnetism for the 3Q structure the Zeeman formalism needs to be extended to the non-collinear case.

Surprisingly, the nonmagnetic model shows the strongest response to the applied magnetic field with the largest induced moments. As counterintuitive as it may seem, our nonmagnetic model is thus the most magnetic one in terms of bulk net magnetism at 6 T. A plausible explanation is that the metastable nonmagnetic state in the DFT model is more easily perturbed by the magnetic field.

Regardless, all DFT calculations produce induced magnetic moments that comfortably fall below the proposed upper constraint [13], indicating the DFT model's consistency with the experiments.

IV. Conclusions

For the last couple of decades, a lot of effort has been devoted, both experimentally and theoretically, to try and understand the fascinating, but complex and counterintuitive behaviors of plutonium metal. From a theoretical and conceptual standpoint, there is debate over the nature of the 5f electrons, whose presence in plutonium is believed to be the source of its many facets. On one hand, the concept of localization or partial localization of the 5f electrons make sense in explaining the relatively large atomic volume of the δ phase (25% larger than the α phase) [26]. On the other hand, a delocalized character of the 5f electrons reproduces the δ volume but also provides a consistent picture of the entire phase diagram and many other properties of plutonium [18].

Magnetism is often coupled to the more general question of electron localization. Electron localization-delocalization likely appears in cerium (between the α and γ phase) [2], and certainly happens under compression in the rare-earth elements [27], or even in the heavier actinides [28]. The conventional idea is that as the 4f electrons in the rare earths delocalize with pressure they go through a magnetic collapse. Meaning, a transition where the magnetic moment collapses from a 4f-localized ordered magnetic state to a 4f-delocalized nonmagnetic state. These transitions may happen in conjunction with a volume collapse and a structural transformation because the character of the 4f electrons changes from chemically nonbonding (localized) to bonding (delocalized). Hence, there is a close relationship between magnetism, atomic volume, crystal structure, and the nature of the bonding in f-electron systems. Magnetism is therefore a legitimate issue in plutonium, and it has also been a topic of interest as it relates to the nature of the 5f electrons and the overall understanding of the metal.

When the magnetic form factor was obtained from neutron scattering [23], a picture emerged that points toward magnetic moments in plutonium. These were interpreted as dynamic due to fluctuations [23], a notion that is consistent with the idea of spin fluctuations that has been modeled by magnetic disorder [18, 21]. However, the form factor is equally well represented within a localized [23] and a delocalized [18] model for the 5f electrons and is thus not decisive in guiding the theory.

In the present study of δ plutonium in a magnetic field, we once more reference a case where a magnetic measurement is unable to judge with certainty the theoretical models for plutonium. This is particularly obvious when drastically different approaches such as a nonmagnetic hypothesis and a disordered magnetic hypothesis respond very similarly to the experimental condition. One may suspect that in modest magnetic fields, the magnetic theories would induce large magnetic moments while in the nonmagnetic model much smaller moments would result. Surprisingly, in Table 1 we show that the nonmagnetic model displays a 50% stronger magnetization under the 6 T magnetic field than that of the magnetic models. Nevertheless, all approaches, magnetic or not, are consistent with the results from the experiments [13]. The behaviors of these theoretical models in the presence of a magnetic field highlight the general problem of distinguishing different theories for plutonium on the basis of a magnetic experiment alone. Instead, a holistic view of plutonium where many experimental facts are considered, has to be embraced when evaluating various modeling approaches.

It is interesting that an applied magnetic field on δ plutonium causes a small net induced magnetization where the spin and orbital moments align parallel (the full Zeeman operator). This violates Hund's third rule on a macroscopic level but on each atomic site the magnetic moments could still be antiparallel as dictated by the rule. The neutron scattering measurement of the magnetic form factor probes the local onsite magnetism rather than the net macroscopic magnetization (they would be the same in a perfectly ideal and ferromagnetic material). Therefore, neutron scattering could explore whether the spin and orbital moments are antiparallel or not and if the Hund's third rule is truly broken.

The shape of the measured magnetic form factor for δ plutonium [23] is quite similar to that of the rare-earth metal samarium [29]. Qualitatively, they show a maximum in intensity around 0.3-0.4 of the scattering $\mathbf{Q}$ vectors before approaching zero for small $\mathbf{Q}$ vectors. The reason for this particular shape is that the spin and orbital moments are antiparallel [30] and close in magnitude, in both plutonium and samarium. They are so close in plutonium that it is conceivable that they could effectively cancel each other out [18], a phenomenon that has been experimentally verified in a samarium-aluminum alloy system [31]. On the other hand, if the moments align parallel, as the calculated net magnetization in the magnetic field suggests (Table 1), the magnetic form factor looks completely different [30] and disagrees with the neutron scattering result [23]. Consequently, a nonmagnetic state for plutonium, where antiparallel spin and orbital moments do not exist under any circumstance, cannot reconcile the neutron scattering result [23] even in the presence of a magnetic field.

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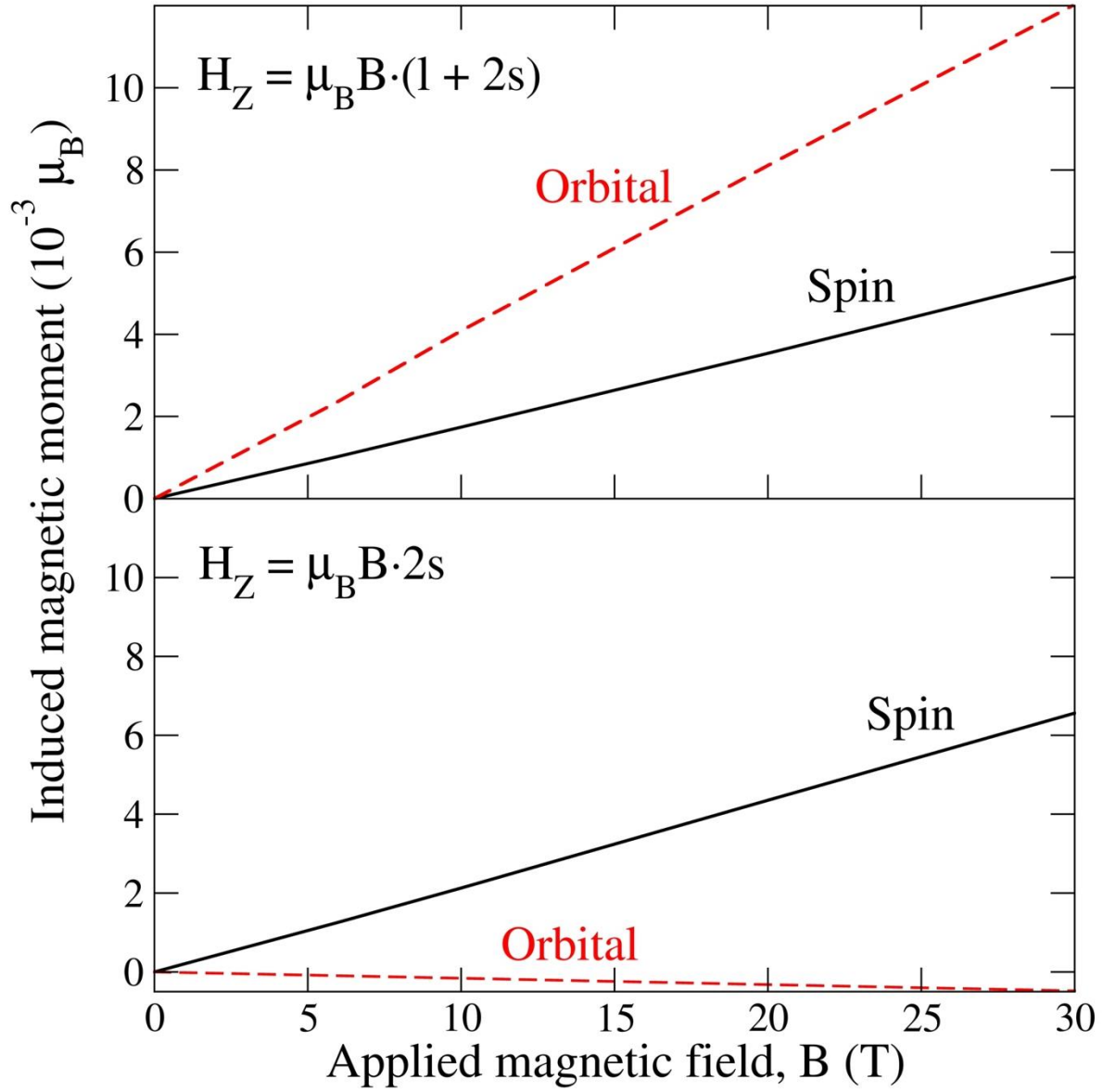


Figure 1. (Upper panel) Calculated induced magnetic spin (solid black) and orbital (dashed red) moments as functions of applied field, assuming the full Zeeman Hamiltonian operator $H_Z = \mu_B \mathbf{B} \cdot (\mathbf{l} + 2\mathbf{s})$. (Lower panel) Induced magnetic spin (solid black) and orbital (dashed red) moments as functions of applied field, calculated with a Zeeman Hamiltonian operator that excludes the orbital coupling term, $H_Z = \mu_B \mathbf{B} \cdot 2\mathbf{s}$. The calculations are for unalloyed δ phase but the atomic volume is that of δ -Pu 2 at.% Ga ($24.7 \text{ \AA}^3$).

Magnetic configuration	Induced spin moment ($10^{-3} \mu_B$)	Induced orbital moment ($10^{-3} \mu_B$)	Induced total moment ($10^{-3} \mu_B$)
Disordered magnetic	1.03	2.38	3.41
Antiferromagnetic	1.06	2.55	3.61
Nonmagnetic	3.58	1.71	5.29

Table 1. Calculated field-induced net magnetization moments at 6 T for δ plutonium. The complete Zeeman operator is considered. The magnetic configurations are disordered magnetic, antiferromagnetic, and nonmagnetic, respectively. All magnetic moments are well below the upper constraint proposed in the experimental analysis ($0.1 \mu_B$) [8]. The calculations are for unalloyed δ phase plutonium but the atomic volume is that of δ -Pu 2 at.% Ga ($24.7 \text{ \AA}^3$).

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