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Search For a Consistent Mean-Field Treatment of Magnetic Properties of Yittrium-Cobalt-5 Under Moderate Hydrostatic Stress

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Search for a consistent mean-field treatment of magnetic properties of YCo_5 under moderate hydrostatic stress

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We explore the use of particular variants of DFT + U and DFT + orbital polarization (OP) to calculate the electronic structure and magnetic properties of YCo_5 under hydrostatic pressures up to $\sim$ 600 kbar. While the specific DFT + U (with U= 0.75 eV) and DFT + OP schemes we employ produce magneto-crystalline anisotropy energies for YCo_5 in good agreement with experiments performed in ambient conditions, our DFT + U results are shown to greatly overestimate the pressure at which a high-spin to low-spin (HS-LS) transition is known to occur. In contrast, our DFT + OP results predict the HS-LS transition to occur at the same stress as DFT, and in better agreement with experiment. This sensitivity suggests that care should be taken when attempting to model magnetic properties with self-interaction and/or correlation corrections to DFT for this and related materials, and highlights the usefulness of moderate pressure as an additional parameter to vary when discriminating between candidate theoretical schemes.

I. INTRODUCTION

The search for permanent magnet materials which are less expensive than those currently in wide use (e.g., variations on $Nd_2Fe_{14}B$ and Sm_2Co_{17}) would greatly benefit from robust predictive models for key figures-of-merit, one of which is the magnetocrystalline anisotropy energy (MAE).[1] This quantity, the energy to rotate the net magnetic moment from easy- to hard-axis directions, is notoriously difficult to predict accurately, due to its sensitive dependence on the details of the electronic states in the neighborhood of the Fermi energy.[2] Indeed, since permanent magnets often involve rare earth elements, predictions are sullied by the general inability of mean-field electronic structure theories to correctly describe narrow-band f-electron states.

Such is the case for the magnets $SmCo_5$ and Sm_2Co_{17}. For these systems, researchers attempting to arrive at a description of the MAE which is sufficiently detailed to allow for the subsequent prediction of changes that would result from atomic substitutions, used a DFT + U scheme in which the self-interaction correction of the narrow-band states is taken into account at a mean-field level.[3,4] Though a primary problem in $SmCo_5$ and Sm_2Co_{17} is the description of the Sm f-bands, adequate post-diction of MAE for the associated simpler systems, YCo_5 and $LaCo_5$, also requires treatments beyond standard DFT, as shown in Refs. 5–7. In the Steinbeck *et al.* work,[6] the application of an orbital polarization[8] correction for the Co-d states was used to bring the predictions of MAE into accord with experiments; if standard DFT is used instead, the MAE for both $LaCo_5$ and YCo_5 are too low by a factor of ~ 5.[6]

While sensitive to the detailed treatment of narrow-band electronic states, the total magnetic moment and the MAE for a given material at a given pressure and temperature are but two numbers.[9] It can therefore be the case that different beyond-DFT treatments, such as DFT + U and DFT + OP (or even different applications of DFT + U), can give identical results for these few quantities even when details of the predicted electronic structures are quite different. In such instances, it is possible that subtle variations in MAE resulting from atomic substitutions could be predicted differently by these different methods. It is therefore of interest to identify additional features of such systems which can be explored both theoretically and experimentally, to further discriminate between candidate theoretical treatments of electronic structure.

The application of external pressure to a material is another way, besides substitution, to generate a family of systems which are each closely related to the starting material. Though magnetism is generally destroyed at high-pressures, due to the widening of bands which disfavors moment formation, modest stresses can preserve the moments while changing the details of the Fermi surface sufficiently to alter a material's magnetic properties. This is known to be the case in YCo_5 (and is likewise predicted to occur in $LaCo_5$ as well),[10,11] where the application of a few hundred kbar of pressure causes a high-spin to low-spin (HS-LS) transition. This results from a feature in the electronic density of states moving past the Fermi level as P is changed, and is accompanied by a concomitant change in the c/a ratio of this tetragonal material, observed experimentally using x-ray diffraction.[11] Thus, even though measurements of, say, the magnetic moment were not possible under pressure, the strong structural signature provided a validation of the theoretical prediction[10,11] of the HS-LS transition in YCo_5. More recent experimental/theoretical investigations of Sm_2Co_{17} have been performed in which local moments were inferred under pressure with an x-ray spectroscopic technique,[12] though no structural transition was found in this case. In both of these studies, it is likely that the moderate pressures involved render the conclusions potentially useful for the better understanding of electronic and magnetic properties of these materials at ambient pressure.

In this work, we explore the use of particular variants of both DFT + U and DFT + OP in the prediction of magnetic and structural properties of YCo_5, in the search for a single theoretical description which agrees with both: 1. The experimental results for the HS $\longrightarrow$ LS transition, and 2. The MAE of YCo_5 at ambient conditions. We find that the DFT + OP treatment, outlined in Ref. 8 and applied to YCo_5 in Ref. 6, gives a good description of the ambient-P MAE while also predicting the occurrence of the HS-LS transition in the same location as that of DFT (which itself is in reasonable accord with experiments[11]). In contrast, our use of DFT + U within the rotationally-invariant scheme outlined in Dudarev *et al.*[13] predicts a HS-LS transition which increases in pressure greatly with U; for the value of U needed to match the experimentally-derived ambient-P MAE, the HS-LS transition is pushed far outside the regime of where it is found experimentally.[11] In this sense, we highlight the utility of moderate hydrostatic stress as a tool for the further understanding of electronic and magnetic properties of YCo_5 and related permanent magnet materials.

In what follows, we describe the computational schemes employed (Sect. II), and present and discuss our results (Sect. III).

II. COMPUTATIONAL DETAILS

A. DFT

Density functional theory (DFT) calculations for YCo_5 were performed with the projector augmented wave (PAW) method[15] as implemented in the Vienna ab-initio simulation package[14] (VASP). Since the pressures we consider are moderate, and represent changes in density of no more than 25%, the Y and Co PAWs designed for ambient conditions are adequate. The bulk of our calculations are performed with the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation to the exchange-correlation functional,[17] but a few calculations are performed within the local density approximation (LDA) as well,[18] for comparison. In all cases, the PAW potentials are chosen appropriately, depending on the exchange-correlation functional, and the kinetic energy cut-offs are chosen conservatively, given the potentials used. For select calculations, we also use a full-potential linear muffin-tin orbital (FP-LMTO) electronic structure code,[16] as discussed below.

With the VASP code, we perform calculations of the dependence of the unit cell geometry on pressure, the pressure-volume relation (i.e., the equation of state), the electron magnetic moments (including both spin and orbital moments), and the MAE, obtained as the difference in total energies between calculations in which the spin polarization direction is constrained to be parallel and perpendicular to the c-axis, respectively. Since MAE is the result of an interplay between crystal-field effects and the spin-orbit interaction, our calculations of this quantity make use of the fully non-collinear 2-component spinor Pauli equation mode of VASP.[19] The MAE is particularly sensitive to the choice of **k**-points;[2] most of our calculations of MAE are performed with a $13 \times 13 \times 13$-mesh, but select convergence tests were also performed for meshes as large as $35 \times 35 \times 35$ by exploiting crystal symmetry.[20]

Our computation of the HS $\rightarrow$ LS and associated first-order structural transition[11] was performed using VASP in two ways: 1. With its built-in structural optimization capability using a conjugate-gradient technique, and 2. By varying the c/a ratio "by hand" at every cell volume. This we did to ensure that the structural optimization method was not getting stuck in local energy minima; in all cases, we found identical optimized structures using both approaches. All of our calculations, be they of magnetic moments, cell shapes, pressure-volume relations, or MAE are performed at $T = 0$.[21]

B. DFT + U

Our computations using DFT + U employ the so-called rotationally-invariant scheme of Dudarev *et al.*.[13] Here, the U we quote corresponds to the $\bar{\mathrm{U}} - \bar{\mathrm{J}}$ in their work, where $\bar{\mathrm{U}}$ is an on-site Coulomb energy and $\bar{\mathrm{J}}$ is an exchange energy. Motivated by the work of Steinbeck *et al.* using DFT + OP,[6] we choose the Co-d states (not the Y-d states) to be those for which the U is applied, though we also perform sensitivity studies in which a U for the Y-d orbitals is included as well (resulting in minimal effects). As mandated by the implementation in VASP, the initial occupation matrix of each spin channel of the Co-d manifold, at the first iteration towards self-consistency, is proportional to the identity, representing an equal and incoherent superposition of these levels.

C. Orbital polarization

The DFT + OP scheme we employ is equivalent to that described in Ref. 8. Here, the satisfaction of Hund's second rule is encouraged by the addition of a term in the electronic Hamiltonian which is proportional to the square of the (in this case Co) orbital moment. This inclusion is motivated by the electronic structure of individual atoms; its use in a solid is not strictly justified, though favorable results have been obtained for systems for which complex multiplet physics is missing in the associated LDA or GGA treatments. The factors analogous to U in this method are the Racah parameters.[8] For YCo_5, we take these directly from the work of Steinbeck *et al.*[6] The Co Racah parameters, which are the most relevant for the calculation of MAE, vary from 132 to 148 meV, depending upon the atomic site within the unit cell.

Since we are concerned with YCo_5 under pressure, it is important to recognize that the appropriate values of both U and the Racah parameters may change with compression. As mentioned, however, our interest is in compressions which are sufficiently moderate so that these changes are expected to be quite small. To check this explicitly in the case of DFT + OP, we used the FP-LMTO code of Ref. 16 to compute the Racah parameters self-consistently for YCo_5, throughout a range of pressures from 0 to 600 kbar. The computed increase in the average value of the Co Racah parameters at 600 kbar relative to those at 0 kbar was $\sim 10\%$. We have verified that such an increase does not change in any way the conclusions that we draw in this work. Thus, we choose both the Racah parameters and the U to be pressure-independent in what follows. A recent study involving the pressure dependence of U parameters for a DFT + U treatment of Sm_2Co_{17} reached similar conclusions.[12]

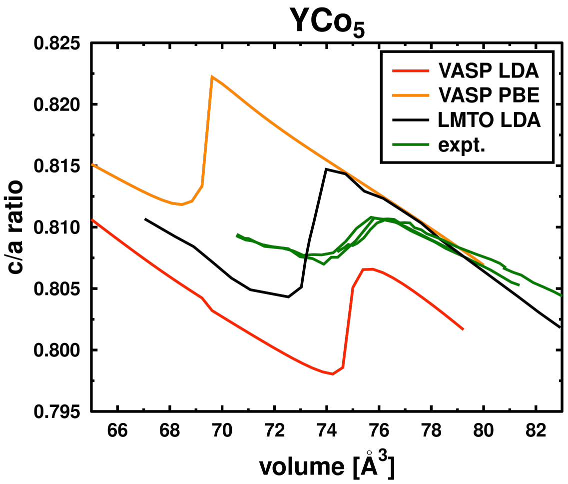

FIG. 1. The c/a ratio vs. cell volume (cell= one formula unit) for YCo_5. Green curves indicate the experimental result from Ref. 11. Black curve shows the theoretical result using LDA, also from Ref. 11. Red and orange curves are our predictions using LDA and PBE, respectively.

III. RESULTS AND DISCUSSION

A. LDA vs. PBE

Before presenting the main results of this work which pertain to the comparison of properties computed with DFT + U and DFT + OP for YCo_5, we discuss DFT results with LDA and PBE exchange-correlation functionals. Figure 1 shows the optimized c/a ratio as a function of unit cell volume, V. The green curve is the experimental result from Ref. 11. The black curve is the theoretical result from the same work, obtained with LDA and an LMTO method. Though the agreement between these two is not perfect, the general behavior is reproduced. These curves show a transition between two separate branches of behavior for the manner in which c/a varies with V. For $V \gtrsim 75$ Å^3, the magnetic moment is large; for $V \lesssim 75$ Å^3, the magnetic moment drops substantially (see Fig. 3 of Ref. 11). This is the HS-LS transition. As explained in Ref. 11, and as predicted earlier in Ref. 10, it results from a change in the topology of the Fermi surface due to the movement of a feature in the partial density of electronic states derived primarily from Co-d orbitals (see Figs. 10 and 11 of Ref.11). We will return to this issue in Sect. III C. The red curve is our LDA result with the VASP code. It is somewhat troubling that it is not in better agreement with the earlier LDA result (black); we do not know the reason for the discrepancy, though we are confident that our results are well-converged within the method we employ. Again,

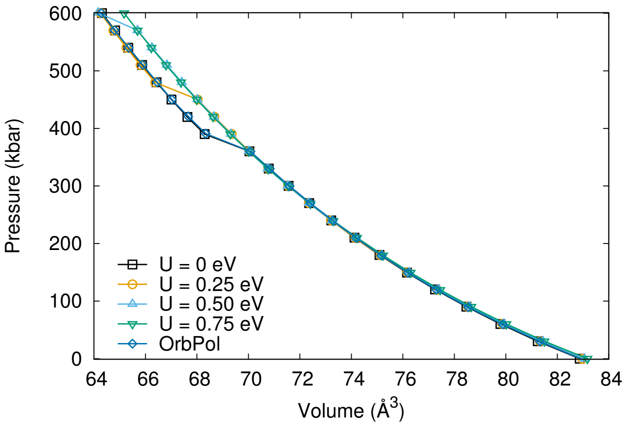

FIG. 2. Pressure as a function of cell volume for YCo_5 as computed by PBE DFT (U= 0.0), and PBE DFT + U (the value of U indicated in the key). The PBE DFT + OP result is also shown.

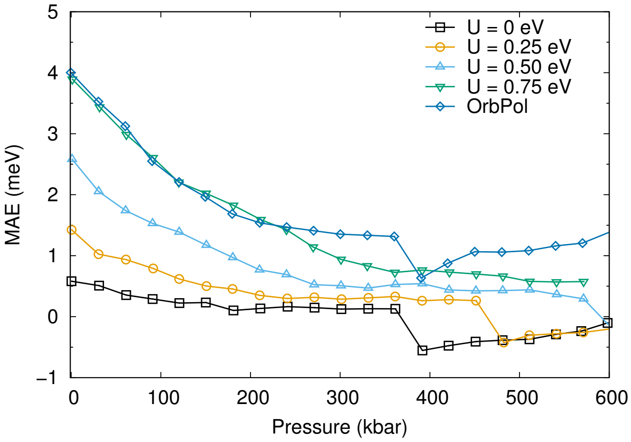

FIG. 3. Magneto-crystalline anisotropy energy per cell vs. pressure for YCo_5 as computed by PBE DFT (U = 0.0), and PBE DFT + U (the value of U indicated in the key). The PBE DFT + OP result is also shown.

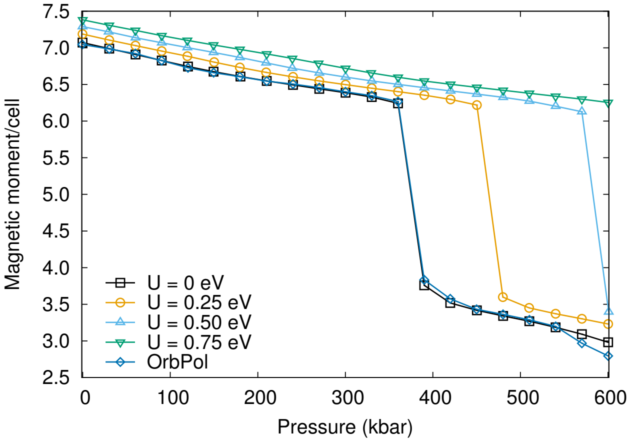

FIG. 4. total spin moment per cell vs. pressure for YCo_5 as computed by PBE DFT (U= 0.0), and PBE DFT + U (the value of U indicated in the key). The PBE DFT + OP result is also shown. The contribution of Y to the total spin moment is negligible in comparison to those of the Co.

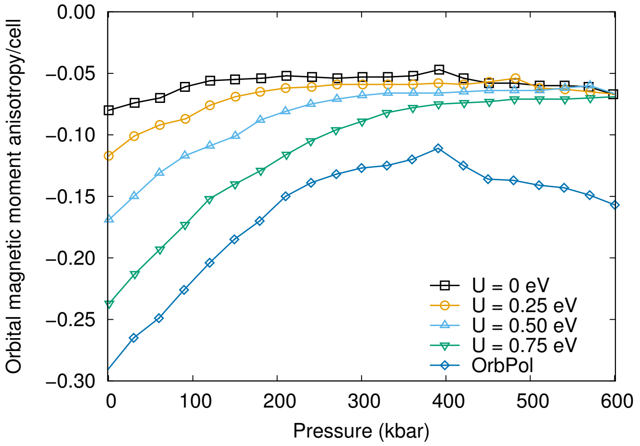

FIG. 5. Orbital magnetic moment anisotropies as a function of pressure for PBE+U and orbital polarization.

however, the general agreement with the experimental result, particularly the V at which the transition occurs, is quite good. The orange curve is our result using PBE exchange-correlation functional. The HS-LS transition is pushed to $V \sim 70$ Å^3.

While this is in worse agreement with experiment than that produced with LDA, the $P(V)$ relation (e.g., the $T = 0$ equation of state) as predicted by PBE is in far better agreement with experiment than is LDA. This is apparent by comparing the experimental equilibrium volume, 83.96 Å^3 of Ref. 25; our LDA result is roughly 10% smaller. For this reason, we use PBE throughout the rest of this work. Though the HS-LS transition appears at lower volume than experiment by $\sim$5 Å^3, we assert that our main conclusions regarding our uses of DFT + U and DFT + OP to predict both the HS-LS transition and the MAE at ambient pressures are insensitive to this choice. Our calculations of the $P(V)$ relation at $T = 0$[21] are shown in Fig. 2, where the PBE result is that indicated by U = 0 eV (black line). Here, the optimized value of c/a is used in the prediction of P for each V. In our PBE calculations, the HS-LS transition occurs at $P \sim 380$ kbar, as indicated by the position of the volume-change in this figure; however if we use the experimental transition-V from Fig.1,[11] the PBE curve of Fig. 2 indi-

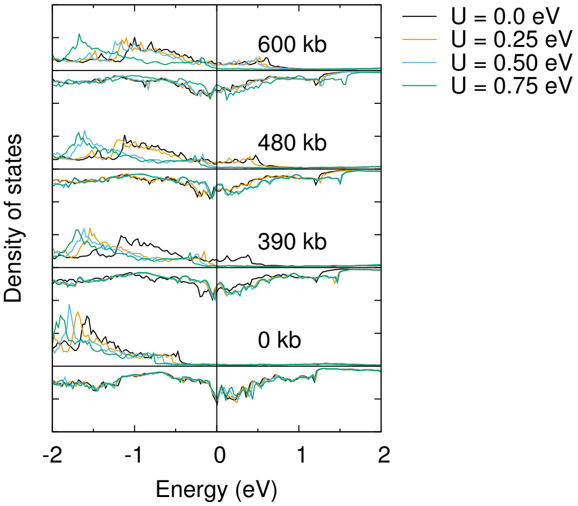

FIG. 6. Co d-projected densities of states for a range of pressures and values of the U parameter. Spin-up (above the horizontal axes) and spin-down (below the horizontal axes) partial densities of states are both shown)

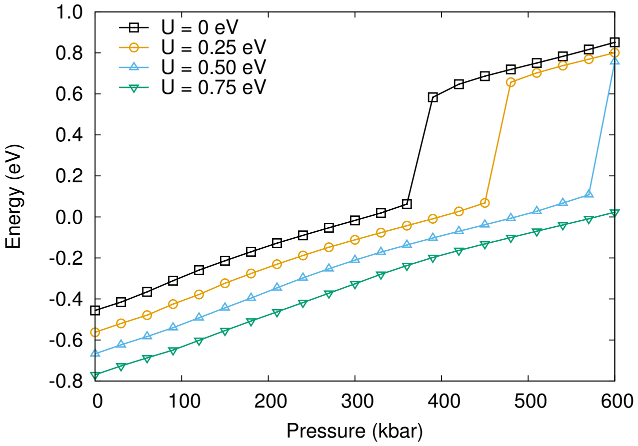

FIG. 7. Energy with respect to the Fermi level at the Γ-point of the most energetic Co-3d spin-up state as a function of pressure and U parameter. Compare with the position of the most energetic spin-up peak in Figure 6. (Orbital polarization coincides with U=0)

cates that its location would be $P \sim$ 200 kbar, in good agreement with experiment. We discuss the remainder of the curves in Fig. 2 below. These results are all produced with the collinear formulation of DFT; the inclusion of spin-orbit produces negligible changes to these c/a vs. V and P vs. V predictions.

Our predictions of the MAE at ambient conditions use the non-collinear formulation in which spin-orbit is included. Our results using LDA are smaller than those of Steinbeck *et al.*:[6] 0.58 meV/cell (we obtain 0.015 meV/cell for the experimental structure and -0.942 meV/cell for 0 kbar). Our PBE result for 0 kbar is 0.582 meV/cell. The huge discrepancy between these numbers and the experimental value of 3.8 meV/cell[22] is what prompted Steinbeck *et al.* to explore the use of DFT + OP for this system. We now consider its use, along with the rotationally invariant DFT + U formulation, in what follows.

B. Magnetocrystalline anisotropy energy with orbital dependent functionals

Motivated by the earlier application of DFT + OP to the prediction of MAE for YCo_5,[6] in which the C-d Racah parameters were found to be substantially more impactful than those of Y, we apply the U-term of (PBE) DFT + U to the Co-d manifold. Within the scheme of Dudarev *et al.*,[13] there is a single U parameter ($\bar{U} - \bar{J}$) which needs to be specified. Instead of computing this parameter self-consistently, as in the treatment of Ref. 23 for instance, we choose to fit the value of U to reproduce, approximately, the experimental value of the MAE of YCo_5 at ambient conditions. This is consistent with our aim in this work, in that it allows us to explore the consequences of this choice for other properties as well. Figure 3 shows the MAE computed for a range of U values, and for a range of pressures from 0 to 600 kbar. U = 0 produces a $P = 0$ MAE of $\sim$ 0.58 meV/cell, as stated above. Larger U values produce successively larger MAE values, with U= 0.75 eV giving rise to a $P = 0$ MAE of $\sim$ 4 meV/cell, very close to the experimental result.[6,22] The general trend of MAE with increasing P is similar for all values of U: A moderate decrease with P in the HS phase, followed by an abrupt small decrease to the value in the LS phase (the abrupt decrease is at $P \sim$ 400 kbar in our U= 0 PBE result; if we appeal to the LDA value for the HS-LS transition volume, this is would be closer to 200 kbar).

Our results for the MAE using (PBE) DFT + OP are shown in Fig. 3 as the dark blue curve. Note that it is nearly coincident with that of DFT + U=0.75 eV (green curve) throughout the entire field of stability of the HS phase, not just at $P = 0$. While we know of no measurements of MAE for this material at elevated pressures, we have established that this particular variant of DFT + U with U= 0.75 eV gives identical results for the the $P = 0$ MAE of YCo_5 to both that of LDA + OP[6] and experiment.[22]

Looking back to Fig. 2, we see that the $P(V)$ relations of the HS and LS phases are, individually, unaffected by the application of either the U in DFT + U or the OP term. In this sense, the equation of state itself, and in particular the value of the equilibrium density of YCo_5 at ambient conditions, is insensitive to the use of these particular beyond-DFT additions. Only the location of the HS-LS transition itself is affected, as seen in the upper-left portion of figPV. We now discuss this further.

C. Pressure-induced high-spin to low-spin transition

Figure 4 shows our computed total spin magnetic moments versus P for the DFT + U and DFT + OP treatments we have employed. We first discuss the values of the spin moments at $P = 0$ (i.e., in the HS phase). As also noted in Ref. 6, we find that the spin moment is largely unaffected by the OP term, as evidenced by the coincidence of the PBE moments (labeled U = 0 eV) and the PBE + OP moments (labeled OrbPol). Instead, the OP term enhances the value of the *orbital* moment, as per its design; the orbital moments are however far smaller than the spin moments.[6] This is further illustrated in Fig. 5, where it is shown that the *anisotropies* of the orbital moments increase with increasing U and also with the application of OP. In contrast, on the scale of Fig. 5, the spin moment anisotropies are negligible.

Our PBE value for the total spin moment at $P = 0$ is $\sim$ 7.1 Bohr/cell, somewhat smaller than the LDA result of Steinbeck *et al.*,[6] 7.3 Bohr/cell. This is curious, given the general trend for PBE moments to be larger than LDA moments, indicating potential differences in the underlying methodologies of the codes we employ. Nevertheless, these are in the neighborhood of the experimentally inferred total spin moment of 6.94 Bohr/cell.[6,24] We find that for the DFT + U scheme applied to the Co-d states as discussed above, the $P = 0$ spin moments increase to 7.5 Bohr/cell for U= 1.0 eV, pushing the value further still from the experimental result.

More significant, however, is the affect of the U term on the location of the HS-LS transition. This transition is indicated in Fig. 4 by the precipitous drop in the spin moment from $\sim$ 6.5 Bohr/cell on the HS side to $\sim$ 3.5 Bohr/cell on the LS side. As U is increased, the HS-LS transition moves in its location from $P \sim$ 400 kbar (U= 0.0) to $P \sim$ 600 kbar (U= 0.5 eV), with further increases in P as U is raised beyond 0.5 eV. Even if the correct location of the HS-LS transition in V is imposed upon these results to decrease the transition-P as discussed above, its predicted DFT + U value for U $> 0.25eV$ is in contradiction with the experimental value of $\sim$ 200 kbar.[11] And more specifically, the value of U needed to match the ambient-P MAE, U= 0.75 eV, is clearly excluded, given that the HS-LS transition would then be in the Mbar range. These observations lead us to conclude that DFT + OP as applied to the Co-d manifold is a better scheme to employ when compared to the rotationally-invariant version of DFT + U for YCo_5, if both the MAE and the prediction of its dependence on potential structural variations are of interest. We add that while the specific results we present here are based on a PBE DFT starting point, these same qualitative conclusions are valid from an LDA starting point as well; in that case, HS-LS transition volumes are better predicted, at the expense of a far less accurate $P(V)$ relationship.

To better understand the reason for the qualitative difference in the predicted HS-LS transition when comparing DFT + U and DFT + OP, Fig. 6 shows the spin projected density-of-states for several values of U and for a few representative pressures. In agreement with Koudela *et al.*, we see that the HS-LS transition is associated with partial vs. full occupancy of the majority spin of the Co d shell. Once the most energetic Co d-peak (at approximately -0.5 eV for $P = 0$) moves through the Fermi level, the transition is induced. Note that for the sake of clarity, we have not included the OP DOS in this figure as it can be seen to be virtually identical to the $U = 0$ case. The clear correlation of the crossing of this level with the Fermi level and the HS-LS transition is further elucidated in Fig. 7.

IV. CONCLUSIONS

We have explored the use of both particular variants of DFT + U[13] and DFT + orbital polarization[5,6,8] in the prediction of properties of the permanent magnet material, YCo_5. Our aim was to identify a single treatment capable of: 1. Reproducing the correct value of the magneto-crystalline anisotropy energy at ambient conditions, and 2. Reproducing the location of the magneto-structural high-spin to low-spin transition at elevated pressures. While DFT + OP was established years ago as a viable approach to address the first concern,[5,6] we have here argued that its application is also consistent with the experimental results for the HS-LS transition.[11] This results from the fact that its predictions for this magneto-structural property are nearly coincident with those of straight DFT, which is in turn is in reasonable accord with experiments. In contrast, the application of DFT + U using the scheme of Ref. 13, while producing similar results for the MAE as long as a suitable value for U is chosen, fails to correctly describe the location of the HS-LS transition in this material. In the application of both approaches, the same set of Co-d states was used for the orbital-dependent corrections.

We hope that this stands as a cautionary tale for researchers engaged in the prediction of permanent magnet properties, since DFT + U schemes have been used extensively in such materials (see, e.g., Refs. 3, 4, and 12). We hasten to add, however, that many such treatments have been applied to the f-states of rare earth elements such as Sm and Nd, rather than to the the wider-bandwidth Co-d states in this and related works. In other cases, DFT + U may very well be appropriate. Furthermore, it is likely that more nuanced uses of the general DFT + U methodology, beyond those employing a single parameter U, may better represent the true d- and f-electron multiplet physics necessary to describe magnetic properties. Even in such cases, however, it is likely that careful study will be needed to determine if robust magnetic properties can be predicted when these more involved approaches are used.[26]

V. ACKNOWLEDGEMENTS

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