Spin and Orbital Magnetic State of UGe_2 under Pressure

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The correlated band theory picture (LSDA+U) has been applied to UGe_2, in which superconductivity has been found to coexist with robust ferromagnetism. Over a range of volumes (*i.e.* pressures), *two* nearly degenerate states are obtained, which differ most strikingly in their orbital moment (on uranium) character. The calculated moment, and its separation into spin and orbital parts, is consistent with one set of recent polarized neutron scattering data. These two states are strong candidates for the two ferromagnetic phases, one low-temperature – low-pressure, the other higher-temperature – higher pressure. Orbital (and spin) waves built from fluctuations between these uranium configurations provide a possible novel mechanism of pairing in UGe_2.

I. INTRODUCTION

The possibility of coexistence of superconductivity (SC) and ferromagnetism (FM) has long been of theoretical interest. However, the predominance of spin-singlet SC, together with the evident competition between singlet SC and FM, led to the accepted view that SC and FM order are mutually exclusive. Recent experiments discovered SC and FM coexistence in UGe_2[1], URhGe[2], and $ZrZn_2$[3] restoring theoretical interest in the problem. Both the experiment and the theory favor parallel spin pairing, magnetically mediated SC in these materials, but no microscopic material specific theory of SC-FM coexistence exists at this time.

We focus here on the case of UGe_2, for which SC occurs in the pressure (P) range of 1.0 – 1.6 GPa (10 – 16 kBar). A very interesting feature of this material is an additional (to FM and SC ordering) phase transition (or rapid crossover) which appears as a jump in the magnetization[4]. This magnetic moment vs pressure change has been interpreted by Sandeman, Lonzarich, and Schofield[5] as a first-order Stoner-like phase transition in spin-only magnetization due to a sharp double-peak density of states (DOS) very near the Fermi level. We show here, using electronic structure methods that account for modest, but important intraatomic correlation effects, that the change in the magnetization is associated with the change of the uranium contribution to both the orbital and spin magnetic moments, of which the orbital component is larger and appears to be the more interesting contribution. Our calculational results suggest a new explanation of the magnetic phase transition intimately involving a change of the U orbital state in UGe_2 with pressure and temperature. The related orbital fluctuations can also provide a natural microscopic pairing mechanism, thereby tying the itinerant $5f$ electron superconductivity to the $5f$ spin and orbital magnetism.

II. COMPUTATIONAL METHOD AND RESULTS

Recent experiments on single crystals[7,8] indicate UGe_2 to have the base-centered orthorhombic $ZrGa_2$ crystal structure ($Cmmm$). The structure, shown in Fig. 1, can be viewed as consisting of antiphase zigzag chains of U atoms running along the $\hat{a}$ direction and lying within the $\hat{a} - \hat{b}$ plane; however, interchain and intrachain U-U distances are comparable. Each U atom is tenfold coordinated by Ge. Importantly, the structure possesses inversion symmetry: without it, a FM system will not support zero-momentum Cooper pairs. Single crystal magnetization measurements[6], neutron powder diffraction measurements[7], and very recent single crystal polarized neutrons measurements[8] yield a collinear magnetic structure with ferromagnetically ordered magnetic moment of 1.42 – 1.5 μ_B. (We quote moments per formula unit, *i.e.* per U atom.) The Curie temperature $T_c = 52$ K at ambient pressure decreases with pressure, and vanishes

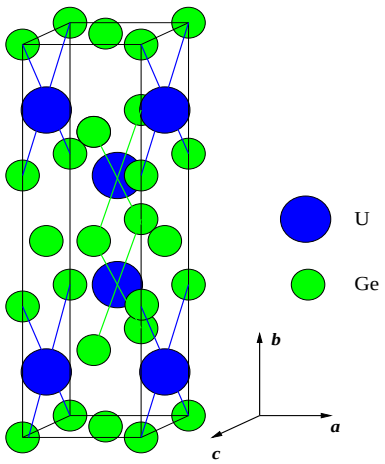

FIG. 1: The base centered orthorhombic $Cmmm$ crystal structure of UGe_2. The volume shown includes two primitive cells.

at 1.6 GPa. Around 1 GPa, Saxena *et al.*[1] and Huxley *et al.*[9] have found that UGe_2 becomes superconducting while remaining strongly ferromagnetic (saturation magnetization $\bar{M} \approx 1\ \mu_B$/U), and thereby providing the first and still the best example of coexistence of superconductivity with robust ferromagnetism.

Here, we use the correlated band theory (LSDA+U) method, which consists of the local spin-density approximation (LSDA) augmented by a correcting energy of a multiband Hubbard type and a self-interaction subtraction term. The LSDA+U method can be regarded as the static limit of the LSDA combined with the dynamical mean field theory (LSDA+DMFT). The full-potential linearized augmented plane-wave (FP-LAPW) method including spin-orbit coupling (SOC) is used to calculate the total energy and the spin and orbital magnetic moments, and their dependence on pressure, for a normal state of UGe_2 at T=0. When the SOC is taken into account, the spin is no longer a good quantum number, and the electron-electron interaction energy E^{ee} in the LSDA+U total-energy functional[10] has to be modified. We use the generalization[11],

$$E^{ee} = \frac{1}{2} \sum_{\gamma_1\gamma_2\gamma_3\gamma_4} n_{\gamma_1\gamma_2} \Big(V^{ee}_{\gamma_1\gamma_3;\gamma_2\gamma_4} - V^{ee}_{\gamma_1\gamma_3;\gamma_4\gamma_2} \Big) n_{\gamma_3\gamma_4} \ , (1)$$

where V^{ee} is an effective on-site Coulomb interaction, expressed in terms of Slater integrals (see Ref. 13, Eq.(3)) which are linked to intra-atomic repulsion U and exchange J . The essential feature of the total energy functional Eq.(1) is that it contains spin-off-diagonal elements of the on-site occupation matrix $n_{\gamma_1\gamma_2} \equiv n_{m_1\sigma_1,m_2\sigma_2}$ which are in general non-zero in the presence of the SOC.

For the given set of spin-orbitals $\{\phi_{m\sigma}\}$, we then minimize the LSDA+U total energy functional. It gives the Kohn-Sham-equations for a two-component spinor $\Phi_i = \begin{pmatrix} \Phi_i^{\uparrow} \\ \Phi_i^{\downarrow} \end{pmatrix}$[12],

$$\sum_{\beta} \Big(-\nabla^2 + \hat{V}_{eff} + \xi(\vec{l}\cdot\ \tilde{\sigma}) \Big)_{\alpha,\beta} \Phi_i^{\beta}(\mathbf{r}) = e_i \Phi_i^{\alpha}(\mathbf{r}) \ , \quad (2)$$

where the effective potential V_{eff} is the sum of the standard LSDA potential and electron-electron interaction potential V_{+U}:

$$\hat{V}^{\alpha,\beta}_{+U} = \sum_{m,m'} |\phi_{\alpha m}\rangle W^{\alpha m,\beta m'} \langle \phi_{\beta m'}| \quad (3)$$

where,

$$W^{\alpha m,\beta m'} = \sum_{p\sigma,q\sigma'} \Big(\langle m'\beta, p\sigma | V^{ee} | m\alpha, q\sigma' \rangle \ - \quad (4)$$

$$\langle m'\beta, p\sigma | V^{ee} | q\sigma', m\alpha \rangle \Big) n_{p\sigma,q\sigma'} - \delta_{m,m'}\delta_{\beta,\alpha} \Big(U(n \ - \ \frac{1}{2}) - J(n^{\beta} \ - \ \frac{1}{2}) \Big)$$

and the operator $|\phi_{\alpha m}\rangle\langle\phi_{\beta m'}|$ is acting on the two-component spinor wavefunction $|\Phi\rangle$ as $|\phi_{\alpha m}\rangle\langle\phi_{\beta m'}|\Phi^{\beta}\rangle$. We then use the LAPW basis in the way described in Ref. 13 to solve self-consistently the Eq.(2).

We note that the LSDA contributions to the effective potential $\hat{V}_{eff}$ in Eq.(2) (and corresponding terms in the total energy) are corrected to exclude the f-states non-spherical interaction contributions. It allows to avoid the f-states non-spherical Coulomb and exchange energy "double counting" in LSDA and "+U" parts of the effective potential and also corrects the f-states non-spherical self-interaction.

Minimization of the LSDA+U total energy functional Eq. 1 generates not only the ground state energy, but also one-electron energies and states providing the orbital contribution to the magnetic moment. The basic difference of LSDA+U calculations from the LSDA is its explicit dependence on on-site spin and orbitally resolved occupation matrices. The LSDA+U creates in addition to spin-only dependent LSDA potential, the spin and orbitally dependent on-site "+U" potential which produces the orbital polarization. The inclusion of the electron correlation induced orbital polarization beyond that given by the LSDA (where it comes from the spin-orbit coupling only) is necessary in order to obtain the values of spin M_S and orbital M_L magnetic moments[14] consistent with the experiment.

III. TWO NEARLY DEGENERATE STATES

We perform the calculations for different values of the lattice constant a fixing the $c : b : a$ ratios and internal atomic positions as given by experiment[7], and we use Coulomb $U = 0.7$ eV and exchange constant $J = 0.44$ eV[14]. In all calculations we fix the magnetization along the $\hat{a}$ axis (the easy axis)[14] and assume FM ordering. The 144 special k-points in the irreducible 1/4 part of the BZ were used, with Gaussian smearing for k-points weighting. The "muffin-tin" radius values of $R_{MT} = 3.2$ a.u. for U, and $R_{MT} = 2.0$ a.u. for Ge, and $R^{Ge}_{MT} \times K_{max} = 6.5$ (where, K_{max} is the cut-off for LAPW basis set) were used. The charge/spin densities were converged better than 5×10^{-5} electron/(a.u.)^3.

The key feature is that we find *two distinct self-consistent FM solutions* that can be sustained within the LSDA+U procedure; henceforth these states will be referred to as FM1 and FM2. The total energy E vs volume (expressed in terms of the lattice constant a) dependence, shown in Fig. 2, leads to the calculated equilibrium value $a = 7.48$ a.u. for both the FM1 and FM2 states, a value that is in reasonable agreement with experimental $a = 7.55$ – 7.63 a.u. values.[7,8] It is noteworthy that the LSDA+U procedure used here for UGe_2 corrects about a half of the severe overbinding error in LSDA, reducing the underestimate of the volume from 9% to 4 – 5%.

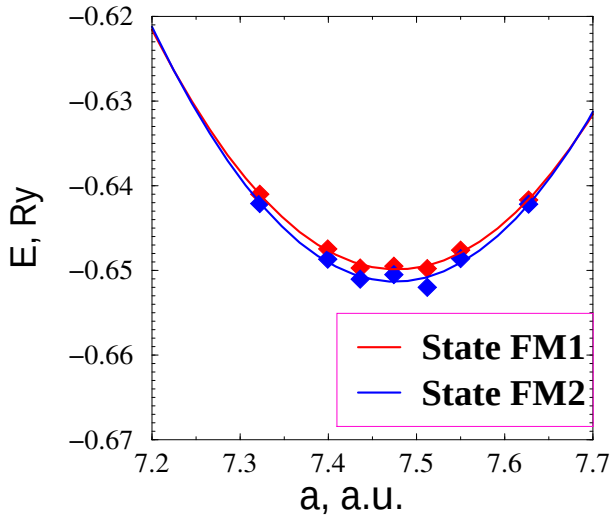

FIG. 2: Total Energy E vs lattice parameter a (see text). State FM1 is slightly higher in energy than state FM2.

The calculated energy difference E(FM1) - E(FM2) $\sim$ 1 mRy/U-atom is very small and decreasing with pressure (see Fig. 2). Because of the small uncertainties in energy differences in LSDA+U calculations, we consider the FM1 and FM2 states to be essentially degenerate within the accuracy of these LSDA+U calculations. The total magnetic moment M_{tot} (per primitive cell and U atom) comprised of the spin M_S + orbital M_L contributions, together with the orbital moment fraction $C_2 = M_L/M_{tot}$ and orbital-to-spin ratio $R_{LS} = |M_L/M_S|$, calculated at the equilibrium lattice parameter a, are given in Table I for the FM1 and FM2 states. We find a good correspondence of our calculated values to the experimental values of M_{tot} and the ratios C_2 and R_{LS}; the agreement is particularly good for the state FM2. Both our calculations and the polarized neutron scattering data[8] clearly demonstrate the presence of a large (practically dominating) orbital magnetic moment on U atom in UGe_2.

TABLE I: The total magnetic moment M_{tot} (spin+orbital) per formula unit, the spin M_S, orbital M_L and total M^{tot} magnetic moments, together with $C_2 = M_L/M_{tot}$ and $R_{LS} = |M_L/M_S|$ ratios for the uranium atom, calculated at the equilibrium lattice constant a for the states FM1 and FM2.

	FM1	FM2	Exp. 8
M_{tot}, μ_B	1.38	1.50	1.5
M_L^U, μ_B	2.98	3.05	
M_S^U, μ_B	-1.56	-1.52	
M_{tot}^U, μ_B	1.42	1.53	1.45
$C_2 = M_L^U/M_{tot}^U$	2.10	2.0	1.81
$R_{LS} = \|M_L^U/M_S^U\|$	1.91	2.0	2.24

We show in Fig. 3 the dependence of M^{tot} on pressure for the states FM1 and FM2. There is roughly 0.2 μ_B difference in M^{tot} between these two states, which originates mainly from the U atom. Then, we can associate our results with Fig. 2(b) of Ref.[4] assuming that the sudden change in magnetization occurs as the system moves from FM2 to FM1 under applied pressure. This is further supported since the magnetic states of UGe_2 are shown experimentally to switch in the applied field of 5T meaning that they are extremely close in energy.

We point out that measurements of the ratio R_{LS} dependence on pressure can be a good way to probe further the origin of the magnetic states in UGe_2, since it is predicted to change rapidly from FM2 (2.0) to FM1 (1.9) in our calculations (see Fig. 4) and this ratio can be measured in polarized neutron diffraction experiments. To date the very limited experimental information on the ratios C_2 and R_{LS} is available. Kuwahara *et al.*[15] reported magnetic form-factor vs pressure measurements at P=0 and 14 kBar and found a slight ($\sim$ 0.1) decrease of C_2-ratio with pressure (from 1.69 to 1.59 for U^{3+}). From the relation $R_{LS} = C_2/(1-C_2)$, these values would lead to the orbital-to-spin ratio R_{LS} from 2.45 to 2.69. Recently, the results of Ref. 15 were complemented by measurements of selected magnetic peak intensities vs temperature at P=0 and 12 kBar Ref.16. These data also indirectly suggest an increase in R_{LS} ratio (by $\sim$ 15 %). Although the experimental data of Ref.[15] do not agree with our calculations, we have to mention that the ambient pressure C_2 and R_{LS} values which they report differ substantially from those of Ref.[8], and accurate experimental determination of the C_2 and R_{LS} ratios under pressure with the desirable accuracy ($\pm$0.1) could be a very difficult task.

We plot in Fig. 5 the partial $5f$ DOS for the FM1

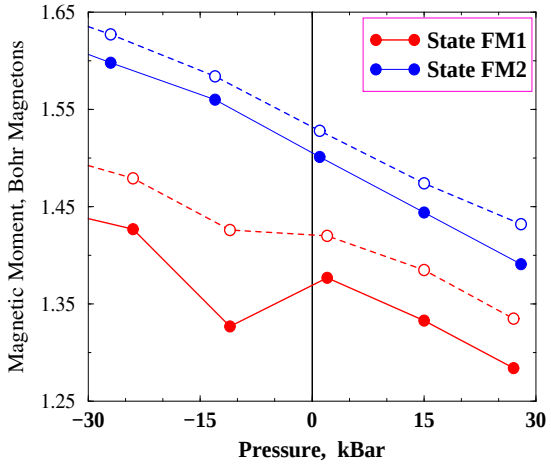

FIG. 3: Pressure dependence of M_{tot} per primitive cell (full line) and M_{tot} per U-atom sphere(dashed line) for the states FM1 (lower pair of curves) and FM2 (upper pair).

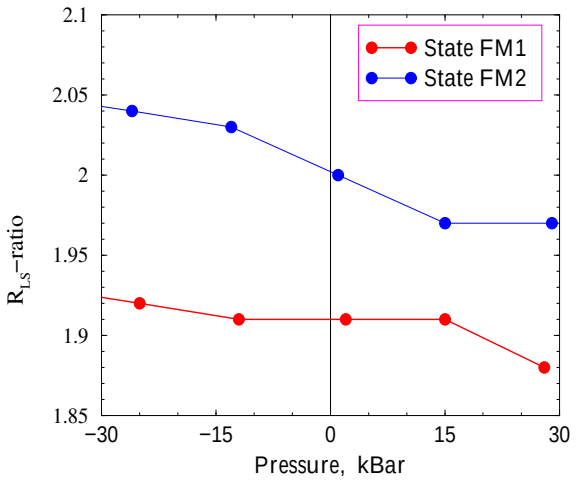

FIG. 4: Pressure dependence of the U-atom ratio $R_{LS} = -M^l/M^s$ for state FM1 (lower curve) and FM2 (upper curve).

state (top) and the FM2 state (bottom) for two different pressures P=–30 kBar and P=0. The major difference between FM1 and FM2 solutions is seen to arise from the difference between the orbital occupation of the states in the vicinity of the Fermi level: FM1 state has the $|\uparrow; m_l = 0\rangle$ level nearly fully occupied, whereas the FM2 state has that state *un*occupied and $|\uparrow; m_l = -1\rangle$ roughly half occupied. With increasing pressure (see Fig. 4b), the mixing of $|\uparrow; m_l = -1\rangle$ and $|\uparrow; m_l = 0\rangle$ levels is increasing for FM2 and its electron configuration becomes closer to that of the FM1 state. This configurational instability could lead to a pronounced change in m_l at a FM2 $\rightarrow$ FM1 transition, causing a step-like change in the M_{tot} under applied pressure.

IV. DISCUSSION

To understand the possible reason for the FM2 $\rightarrow$ FM1 transition, let us first note that it is connected with the changes in the electronic structure in the vicinity of the Fermi level E_F. For our purpose, it is convenient to divide the f-states in two groups (according to their energy positions): "localized" $|\uparrow; m_l = -3\rangle$ and $|\uparrow; m_l = -2\rangle$ which are occupied at all volumes and therefore which will not contribute to the transition, and "itinerant" $|\uparrow; m_l = -1\rangle$ and $|\uparrow; m_l = 0\rangle$ which straddle E_F. (For simplicity, we refer them to as "pure"-spin-$\uparrow$ states, while actually they also have an admixture of spin-$\downarrow$ components due to the SOC). We can then divide the $5f$ fermionic field operator $\hat{\psi} = \hat{\psi}^{loc} + \hat{\psi}^{itn}$ into "localized" (or, more correctly inert) and "itinerant" parts and write a model Hamiltonian as a sum of on-site and intersite contributions:

$$\hat{H} = \sum_{i}^{on-site} \hat{H}^i + \sum_{i \neq j}^{inter-site} \hat{H}_{ij} \qquad (5)$$

Since we assume that the ferromagnetic order is not changed at the FM2 $\rightarrow$ FM1 transition, we do not expect the intersite term to contribute and will consider the on-site term only. We can further write it down as an effective spin-and-orbital Hamiltonian:

$$\hat{H}^i = \hat{H}^{loc}[\vec{S}_{loc}, \vec{L}_{loc}] - J\vec{S}_{loc} \cdot \vec{S}_{itn} \qquad (6)$$
$$+\lambda \vec{S}_{itn} \cdot \vec{L}_{itn} + \frac{1}{2}\vec{L}_{itn} \cdot \overleftrightarrow{\xi} \cdot \vec{L}_{itn}$$

Here, J is an effective positive intra-atomic (or Hund's) exchange coupling between localized $\vec{S}_{loc}$ and itinerant $\vec{S}_{itn}$ spins, λ is the SOC constant, and $\overleftrightarrow{\xi}$ is a crystal field (CF) tensor (we assume for simplicity the crystal field to be quadratic due to the low orthorhombic symmetry). Since we associate the FM2 $\rightarrow$ FM1 transition with the change of the itinerant orbital state, only the last two terms in Eq.(6) are relevant. A further simplification can be naturally made by replacing $\vec{S}_{itn}$ and $\vec{L}_{itn}$ by single-particle $\vec{s}$ and $\vec{l}$ operators.

The energy of the FM2 state (with $|\uparrow; m_l = -1\rangle$) is then given as $E_2 \approx E_\circ - \lambda/2 + |\xi|/2$, and the energy of the FM1 state ($|\uparrow; m_l = 0\rangle$) is $E_1 \approx E_\circ$, where $E_\circ$ is a reference constant energy. It is then clear that the FM2 state is lower in energy than the FM1 state when $\lambda > |\xi|$ (this norm denotes a relevant measure of the size of ξ), otherwise the FM1 state will become lower in the energy.

This simple picture suggests that at a low pressure the SOC wins over the CF energy, keeping the system in the FM2 state. With increase of pressure, the CF increases and the FM2 $\rightarrow$ FM1 transition occurs when the CF wins over the SOC. This scenario is quite plausible since $\lambda \sim 0.2$ eV is comparable with the usual order of magnitude of the ξ for the U-based compounds. This large CF value originates from the $5f$-states hybridization, and is increasing with increase of the pressure while the SOC λ value remains constant.

We note, that the above separation of the f-states into "localized" and "itinerant" follows from the results of the self-consistent calculations, in which all the f-states are equally treated within the framework of the uniform LSDA+U electron interaction model. This effective division is consistent with the experimentally observed low temperature magnetization dependence[16] $M(T) \sim \sqrt{1-(T/T_c)^3}$, which is somewhat intermediate between that found in the archetype d-metal itinerant ferromagnet Ni_3Al[18], $M(T) \sim \sqrt{1-(T/T_c)^2}$, and the flat Brillouin function dependence, typical for the local moment ferromagnets. Here, we also note that the weaker $M(T) \sim T^{3/2}$ spin-wave-like dependence is not found in UGe_2 due to a strong uniaxial MAE.

It was suggested some time ago[19] that superconducting p-wave (triplet) pairing for equal spin states can appear due to longitudinal magnetic fluctuations (paramagnons). However, that theory would also predict SC to occur in the paramagnetic regime with the transition temperature T_{SC} at least as high as in the FM-region, contradicting the experimental data. To overcome the above difficulty, Kirkpatrick and co-workers[20] proposed an enhancement of T_{SC} due to the magnon-to-paramagnon coupling. In fact, the high magnetocrystalline anisotropy of the FM state of UGe_2[14,21] makes the magnons unlikely to drive SC pairing in this material. In this sense, the possibility of the FM2 state $\leftrightarrow$ FM1 state transition can provide an additional orbital-excitation pairing modes (in addition to paramagnons) which may contribute to the T_{SC} pairing or to enhancement of T_{SC} within the FM-phase. It is precisely at the magnetic transition (which we identify with FM1 $\leftrightarrow$ FM2) that these fluctuations become strongest, and it is observed that T_c is maximized at this transition.

To summarize, our LSDA+U calculations indicate the possibility for a quasi orbitally-degenerate ground state to exist in UGe_2 under pressure. The experimentally observed first order magnetic transition is then explained by the FM2 $\rightarrow$ FM1 change, which arises from the change of the orbital state, with both the orbital M_l and spin M_s magnetic moment components contributing to the corresponding sudden magnetization change. These findings can have an important impact on further developments of a material-specific theory for the magnetically mediated SC in UGe_2.

V. ACKNOWLEDGMENTS

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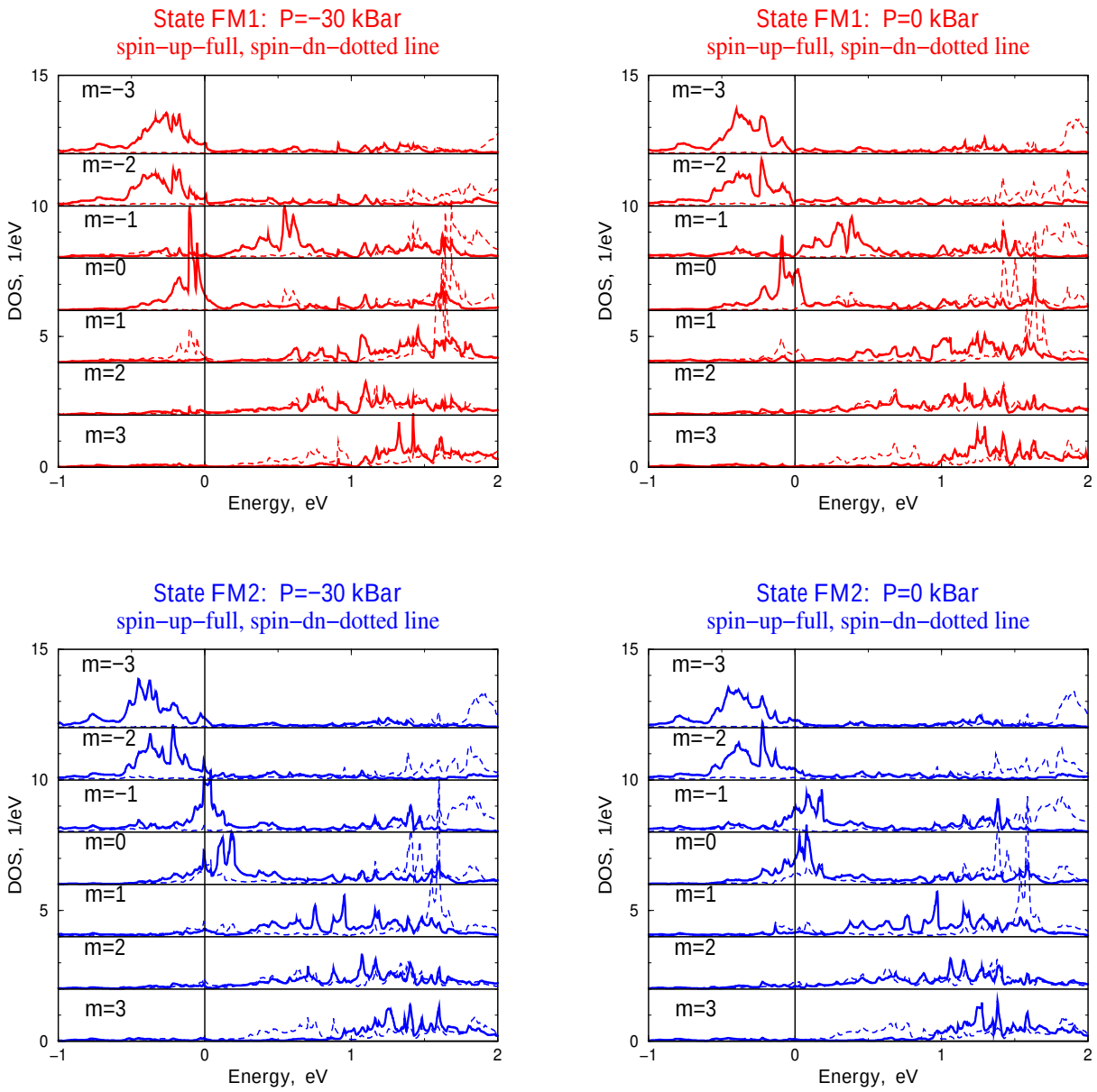

FIG. 5: Spin and orbitally resolved U atom 5f DOS for the states FM1 (red) and FM2 (blue) at two different pressures.