Magnetic Structures of Uranium Compounds: Effects of Relativity and Symmetry

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We report results of calculations that explain the noncollinear magnetic structures observed in U_3P_4 and U_2Pd_2Sn in the itinerant-electron picture. We use the local approximation to spin-density functional theory and the augmented spherical wave method incorporating spin-orbit coupling (SOC) and noncollinear moment arrangements. We show how the relativistic effect of SOC and the different symmetry properties of U_3P_4 and U_2Pd_2Sn cooperate, leading in the case of U_3P_4 to ferromagnetic and in the case of U_2Pd_2Sn to antiferromagnetic noncollinear structures.

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Noncollinear magnetic configurations in insulators, metals, or artificially made multilayers are no exceptions among the observed magnetic structures; see, e.g., Ref. [1]. Early explanations of this phenomenon used essentially the Heisenberg model which, as is well known, assumes the magnetic moments to be localized, being represented by vector observables of constant length firmly attached to a given atom in the crystal and coupled by exchange constants (for a review and further references see, e.g., Ref. [2]).

In an alternative approach, connected originally with names like Slater and Stoner, one describes well-defined atomic magnetic moments in the band picture by treating the itinerant electrons in the self-consistent field supplied by the local approximation to spin-density functional theory (LSDF). Actual calculations in this framework met with impressive success for a great variety of very different elemental metals and compounds [3]. These calculations were initially carried out for systems with collinear (ferromagnetic or antiferromagnetic) order only, but recently the LSDF theory was generalized to deal with noncollinear moment arrangements [4] and was successfully applied to a number of different crystals [4,5] where properties of the interelectron exchange interaction were responsible for the formation of the noncollinear magnetic structure.

It is known that, besides exchange, the relativistic spin-orbit coupling (SOC) can also be responsible for noncollinearity of the magnetic structure even if the SOC is very small as in the $3d$ transition elements [6]. Since the strength of SOC increases rapidly with atomic number, this effect of relativity is expected to play an important role for the type of magnetic order of the heavy elements. In spite of this, no investigation was made to date in the framework of LSDF theory that takes account of both the noncollinearity of the magnetic moments and the spin-orbit coupling. This Letter is supposed to fill this gap with some interesting and new results.

An effective single-particle Hamiltonian that describes both the noncollinearity of the magnetic structure and SOC can be written [7,8] as the sum of two contributions $\hat{\mathbf{H}} = \hat{\mathbf{H}}_1 + \hat{\mathbf{H}}_2$. This Hamiltonian $\hat{\mathbf{H}}_1$ can be derived by minimizing the total energy as a functional of the density matrix [4] and is given by

$$\hat{\mathbf{H}}_1 = -\nabla^2 \mathbf{1} + \sum_\nu \mathbf{U}^+(\theta_\nu, \phi_\nu)\, \mathbf{V}_\nu(\mathbf{r}_\nu)\, \mathbf{U}(\theta_\nu, \phi_\nu). \quad (1)$$

Here $\mathbf{U}(\theta_\nu, \phi_\nu)$ is the standard spin-$\frac{1}{2}$-rotation matrix that describes the transformation between a global and a local coordinate system of the νth atom whose spin orientation is given by the polar angles θ_ν and ϕ_ν with respect to the z axis of the global system. $\mathbf{V}_\nu(\mathbf{r}_\nu)$ is the spin-diagonal effective potential centered at $\mathbf{r}_\nu = \mathbf{r} - \boldsymbol{\tau}_\nu$ in the local frame of reference of the atom at site (ν). The potential is unambiguously given by functional derivatives of the total energy in the LSDF [4] with respect to elements of the density matrix.

The second term of the Hamiltonian, $\hat{\mathbf{H}}_2$, accounts for the SOC and may be written as follows:

$$\hat{\mathbf{H}}_2 = \sum_\nu \mathbf{U}^+(\theta_\nu, \phi_\nu) \left\{ \sum_\alpha M_\alpha \sigma_\alpha \hat{l}_\alpha \right\} \mathbf{U}(\theta_\nu, \phi_\nu). \quad (2)$$

Here σ_α and $\hat{l}_\alpha$ are the Cartesian components of the Pauli spin matrices and the angular momentum, respectively, in the local system, and the coefficients M can be found in Ref. [8]. Diagonalizing the density matrix [4] enables one to determine self-consistent angles and thus new spin-polarized potentials. Following [9] we add to the Hamiltonian the term $\hat{\mathbf{H}}_{\text{orb}} = I_{\text{orb}} L_z \hat{l}_z$ which takes into account interactions responsible for Hund's second rule. Here L_z is the projection of the atomic orbital moment on the local atomic z axis. The parameter I_{orb} was taken to be equal to 2.6 mRyd to reproduce the atomic $5f$ data [9].

Our calculations are done for the ground-state magnetic structure and, for better physical insight, for configurations "nearby." For the former the directions of the atomic moments are varied from iteration to iteration until self-consistency is achieved. For the latter a constrained calculation for a given magnetic configuration is done with the local atomic systems unchanged during the iteration process [10].

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The actual calculations are done with the augmented spherical wave method [11] choosing two compounds, U_3P_4 and U_2Pd_2Sn, for which there is available good experimental evidence on the noncollinearity of their magnetic structures [12,13]. It must be emphasized that these structures (obtained from neutron diffraction experiments) are radically different. In particular, in the case of U_3P_4 [12] the magnetic moments of the individual atoms do not compensate but rather possess a ferromagnetic component along the (111) axis. Unfortunately, precise values of the angles between the magnetic moments could not be uniquely determined in the experiment. In contrast to this structure is that of U_2Pd_2Sn where the magnetic moments of the U atoms [13] compensate, resulting in (antiferromagnetic) zero macroscopic magnetization, and the angles between the moments are predicted to be integer multiples of 90°.

We first consider U_3P_4 and, to determine the easy axis, carry out calculations for ferromagnetic structures with the magnetization directed along the (001) and (111) axes, respectively. In agreement with experiment [14] we obtain a strong magnetocrystalline anisotropy with a relative decrease of the total energy by 0.5 mRy per U atom in the case of the (111) structure. Next, beginning with the self-consistent ferromagnetic (111) structure, we remove the constraint for the moments to be parallel to the (111) direction. Thus free to rotate, the moments deviate from the (111) direction and result in a noncollinear ground-state magnetic configuration shown schematically in Fig. 1. The calculated magnitude of the moment is in good agreement with experiment, and the angle between the moments and the (111) axis was found to be 1.43°.

An explanation of this property is given in Figs. 1 and 2. The U_3P_4 crystal has a bcc lattice with a basis formed by two formula units, i.e., the unit cell consists of 6 U and 8 P atoms. The crystal structure is rather complicated and need not be discussed here in detail. Instead, to illustrate the important symmetry properties it is sufficient to consider the simple picture of Fig. 1 where the projections onto the (111) plane of the positions and the magnetic moments of the six U atoms are shown. To emphasize that the magnetic moments possess components parallel to the (111) axis, we also show the cone formed by the six U moments with the axis of the cone parallel to the (111) direction.

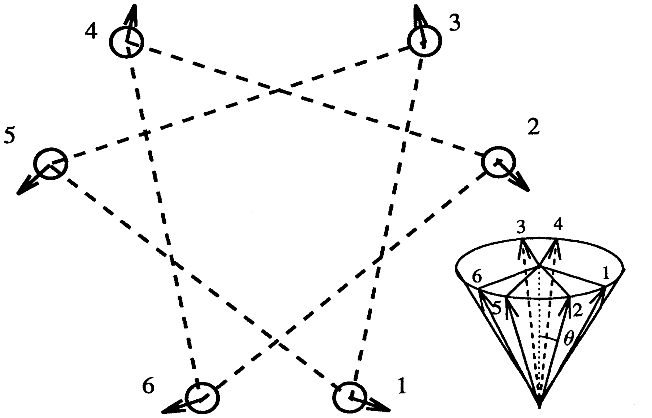

FIG. 1. Projection of the atomic positions and magnetic moments of the U atoms in U_3P_4 onto the (111) plane. At the right the cone formed by the magnetic moments of the U atoms is shown, the cone's axis being parallel to the (111) axis.

For a better understanding of the system's energetics we carried out calculations constraining the directions of the magnetic moments to some values of θ (see Fig. 1 for a definition of θ) near equilibrium. [During the variation of the magnetic structure we keep each moment in the plane containing the ground-state direction of this moment and the (111) axis.] Our results are illustrated in Fig. 2, which shows clearly that the total energy as a function of θ is not symmetric about $\theta = 0$. In fact, for reasons of symmetry no extremum of the total energy at $\theta = 0$ is expected. This can be understood if we consider the symmetry operations that leave invariant both the crystal and the magnetic structures shown in Fig. 1. These operations are the rotations by 120° and 240° about the (111) axis and the reflections in the planes containing the (111) axis accompanied by time reversal. None of these operations leaves the position of any particular atom unchanged. Because of this, symmetry imposes no restrictions on the direction of the magnetic moment of a particular atom but only on the orientation of the atomic moments relative to each other and to the crystal lattice. The deviation of the moments from the (111) axis resulting in a noncollinear magnetic configuration does not change the symmetry of the crystal. Therefore, the ferromagnetic ($\theta = 0$) structure, from a symmetry point of view, is not isolated from structures possessing a finite θ. As a result, the position of the extremum of the the total-energy curve as a function of θ is "accidental," i.e., not determined by the symmetry of the

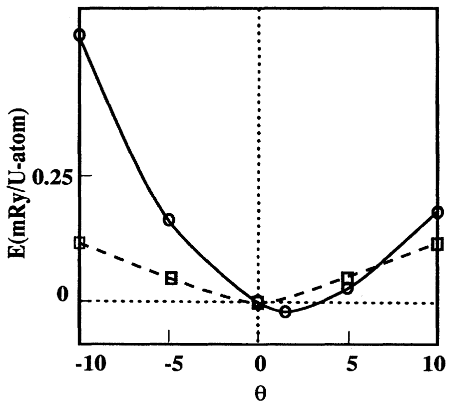

FIG. 2. Total energy of U_3P_4 as a function of angle θ. The solid line was calculated with SOC and the dashed line without SOC.

problem. To demonstrate the crucial role of SOC we show in Fig. 2 the total energy as a function of θ, which we obtain when SOC is neglected in the calculation. Evidently, this curve is symmetric with respect to a change in the sign of θ and possesses a minimum in the total energy for the ferromagnetic structure. The principal difference between these two cases can be easily explained using the technique of spin-space groups (SSG) of operators allowing for independent transformations of the spin and space variables [15]. In the presence of SOC both variables are interconnected, and only operations that transform both the spin and space variables in an identical manner can be symmetry operations; therefore, the spin-space groups give exactly the same description of the symmetry as do the usual space groups. When, however, SOC is neglected, an additional symmetry of the Hamiltonian exists that must be described in terms of the SSG operators. Here it suffices to note that a pure spin rotation of the magnetic moment of every atom by 180° about the (111) axis will transform the positive θ case shown in Fig. 1 to a case with negative θ. This implies that the two structures are equivalent. As a result, the total energy is symmetric about $\theta = 0$. It is interesting to note that the nature of the weak noncollinearity of the magnetic structure in U_3P_4 is similar to the nature of weak ferromagnetism of antiferromagnetic compounds discussed some time ago by Dzialoshinski and Moriya [6]. In both cases, because of SOC, the symmetry of the system does not change when the atomic moments deviate from collinearity.

Unfortunately, although theory and experiment agree completely in that the magnetic structure is noncollinear, the actual value of the deviation of the magnetic moments from the (111) direction obtained in our calculations is much smaller than the only available experimental estimate made in Ref. [12] on the basis of neutron diffraction experiments. At present we have no explanation for this difference.

We next contrast the magnetic order of U_3P_4 with that of U_2Pd_2Sn to which we now turn. Again, for simplicity, we only show the plane of the U atoms in Fig. 3. In the experimental work [13] the results of neutron diffraction experiments were analyzed using the six magnetic structures shown in Fig. 3; the structure labeled NC1 explains the experiments best. It also possesses the lowest total energy in our calculations and supplies a value of the magnetic moment in good agreement with experiment. To demonstrate the importance of SOC in this case, we show in Fig. 4 the dependence of the total energy on the angle ϕ between the magnetic moment of the atom 1 (see Fig. 4) and the x axis calculated with and without SOC. Without SOC all four noncollinear structures are equivalent (and, in fact, to magnetic structures with any arbitrary value of ϕ) because all these structures can be transformed into one another by a pure spin rotation or by a spin rotation plus time reversal. With SOC taken into account this no longer applies; different magnetic configurations, in particular, the configurations NC1–NC4, are nonequivalent, and the electronic properties of the system become ϕ dependent. This ϕ dependence, however, has an interesting symmetry property: equal deviations of ϕ from the value $\phi_0 = 45°$ for NC1 and NC2 and, for NC3 and NC4, from the value of $\phi_0 = 135°$ into opposite directions lead to equal values of the total energy. This "rest symmetry" results from the rotation by 180° about axes of the (110) type (accompanied by time reversal in the case of NC3 and NC4 structures), which remains a symmetry operation also after taking the SOC into account. As a consequence, the total energy has an extremum at

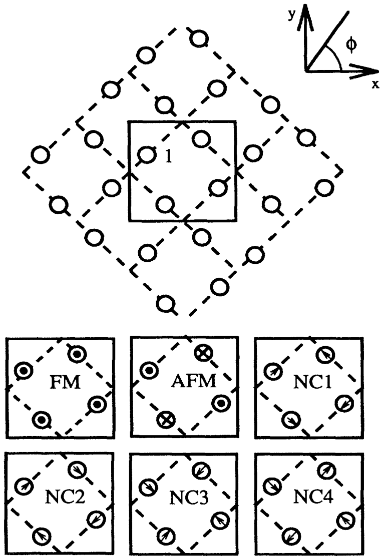

FIG. 3. Plane of the U atoms in U_2Pd_2Sn. The six magnetic structures studied are marked in the figure.

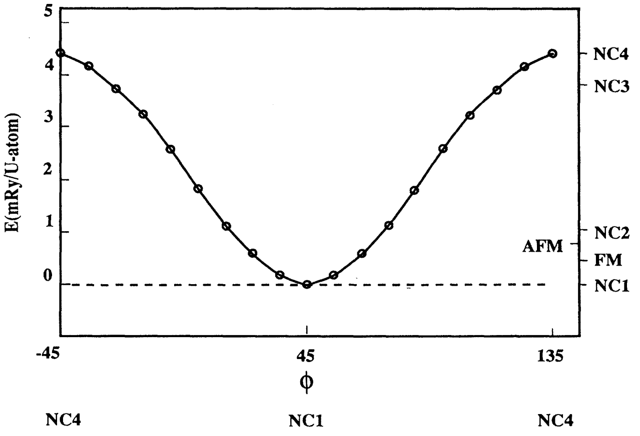

FIG. 4. Total energy of U_2Pd_2Sn as a function of ϕ. The solid line was calculated with SOC and the dashed line without SOC. On the right-hand side the energies of the six magnetic structures (see Fig. 3) are marked.

ϕ_0. Thus in the case of U_2Pd_2Sn the SOC changes the symmetry properties of the Hamiltonian such that the magnetic structure with the lowest energy is isolated by symmetry from the structures obtained by an infinitesimal rotation of atomic moments.

In summary, using a new calculational technique we have shown that the local approximation to spin-density functional theory gives a good description of the complicated magnetic structures in U compounds provided the theory takes into account both noncollinearity and spin-orbit coupling, the latter, relativistic effect being crucial for the formation of the ground-state magnetic structure. Even though, for the two cases studied, the SOC lowers the symmetry of the system, it does so in different ways. In U_3P_4, the SOC leads to a shift of the total-energy minimum to an accidental point that cannot be predicted by symmetry considerations. In the case of U_2Pd_2Sn, however, the SOC lifts a degeneracy and leads to a ground-state magnetic structure that is more symmetric than those obtainable by an infinitesimal rotation of the atomic moments.

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