Noncollinear Intra-atomic Magnetism

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(Received 4 December 1995)

An intra-atomic noncollinear magnetization density has been calculated for the case of ferromagnetic fcc Pu, by means of a newly implemented general-local-spin-density-approximation method which treats the magnetization density as a continuous vector quantity. The presence of noncollinearity is a general effect, not specific to Pu, which is shown to rise due to the interplay of the local exchange and the spin-orbit coupling. The form of the noncollinear part of the magnetization density is very sensitive to the space group symmetry as is demonstrated by calculations with the average spin moment along [001] and [111], respectively. [S0031-9007(96)00401-2]

PACS numbers: 75.25.+z, 71.70.Ej, 75.10.Lp

Noncollinear magnetism (NCM), i.e., magnetic ordering where the different magnetic moments are not parallel or antiparallel to a global direction, exists in a variety of systems. Two well-known kinds of NCM are spiral spin density waves (SSDW) observed, e.g., in the lanthanides and the complex orderings that occur in topologically frustrated antiferromagnets. These types of ordering can be classified as interatomic NCM, as it is the different atomic moments which are noncollinear. Here we demonstrate another type of noncollinearity where the direction of the magnetization density varies on the length scale of an atom. This can arise from either band-structure effects leading to different spin quantization axes for different orbitals on the same atom, e.g., e_g and t_{2g} d orbitals, or, as is demonstrated here, the nontrivial spin mixture produced by the spin-orbit coupling. The present Letter shows that an intra-atomic NCM of the latter form always exists in magnetically ordered systems, even when the atomic moments are collinear. The magnitude of the effect is quantified by a first principles density-functional calculation for fcc Pu, which might be viewed as a simple representative for the large class of magnetic actinide compounds.

Most theoretical work on NCM has been based on the Heisenberg model, but first principles methods [1,2] based on density-functional theory (DFT) that allow for NCM have existed for some years now and have recently attracted a lot of attention. For instance several *ab initio* calculations have been presented for fcc Fe [2–5], where solutions for both SSDW and complex NCM structures have been found. NCM ground states have also been found by means of DFT calculations in more complicated systems; e.g., $MnSn_3$ [6], $ThMn_2$ [7], U_3P_4, U_2Pd_2Sn [8], and $YFe_{12-x}Mo_x$ [9]. Despite the fact that the physical natures of these systems vary considerably it seems clear that DFT calculations are successful in describing their NCM structures and hence provide a powerful tool to study them.

These previous calculations are all based on atomic sphere approximations, i.e., the space is divided into spheres centered around each atom wherein there is only one local spin-quantization axis and the corresponding magnetization density is spherically averaged. In some way these calculations might be viewed as the DFT equivalent of the Heisenberg model as there are well defined local atomic magnetic moments which might point in arbitrary directions, although in these calculations the magnitude of the moment may vary as well. A NCM solution in these cases is found when the different atomic spin-quantization axes are nonparallel; i.e., it is of an interatomic nature.

In a more general spin-dependent DFT [10] the magnetization density is a vector quantity that can vary continuously in direction as well as magnitude all over space. An important question is whether NCM can occur only in terms of nonparallel local magnetic moments or if there might also exist noncollinearity on a smaller length scale within an atom. In principle this could be realized if, e.g., different orbitals, say d and f or even e_g and t_{2g} in a d shell, have different spin-quantization axes. In this Letter we will address this question by showing, by means of DFT calculations within the local spin density approximation (LSDA) in its most general form [10], that when spin-orbit coupling is included there will always exist a noncollinearity in the magnetization density, even within a simple ferromagnet. This is demonstrated explicitly for δ-Pu using self-consistent calculations. This is a new effect caused by the interplay of magnetism and relativity (spin-orbit coupling), which is known already to produce a lot of important phenomena; e.g., it is usually the main contribution to the magnetocrystalline anisotropy, it causes the magneto-optical Kerr effect, and it induces orbital moments in transition metals.

Although originally the LSDA was formulated in a general way with 2×2 density and potential matrices, $\boldsymbol{\rho}(\vec{r})$

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and $\mathbf{v}(\vec{r})$, it has almost entirely been implemented for the special case of diagonal matrices, i.e., collinear magnetization. The charge $\rho(\vec{r})$ and magnetization $\vec{m}(\vec{r})$ parts of the density matrix can be extracted by expanding in terms of Pauli matrices $\boldsymbol{\rho} = \rho\mathbf{1} + \vec{m} \cdot \vec{\boldsymbol{\sigma}}$. In the general LSDA, the exchange-correlation part of the potential $\mathbf{v}_{\mathrm{xc}}(\vec{r}) = v_0(\vec{r})\mathbf{1} + \vec{b}(\vec{r}) \cdot \boldsymbol{\sigma}$ contains nonmagnetic and magnetic parts. The nonmagnetic part v_0 and the magnitude of the magnetic part $\vec{b}$ are given as functions of the local ρ and $|\vec{m}|$ in the same way as in the case of collinear magnetization, but in addition $\vec{b}(\vec{r})$ is always parallel to $\vec{m}(\vec{r})$. The corresponding Pauli-like Kohn-Sham Hamiltonian then looks like (for simplicity the scalar relativistic corrections are for the moment neglected)

$$H = \{-\nabla^2 + v(\vec{r})\}\mathbf{1} + \{\vec{b}(\vec{r}) + \xi\vec{\ell}\} \cdot \vec{\boldsymbol{\sigma}}\,, \qquad (1)$$

where v is the total nonmagnetic part of the potential, ξ is the operator corresponding to the spin-orbit coupling constant, and $\vec{\ell}$ is the angular momentum operator. If the eigenfunctions ψ_i of this Hamiltonian are written in spinor form the magnetization and charge densities can be constructed by summing over the occupied states

$$\vec{m}(\vec{r}) = \sum_i^{\mathrm{occ}} \psi_i^\dagger(\vec{r})\vec{\boldsymbol{\sigma}}\psi_i(\vec{r}), \quad \rho(\vec{r}) = \sum_i^{\mathrm{occ}} \psi_i^\dagger(\vec{r})\psi_i(\vec{r})\,, \quad (2)$$

allowing the usual iterative solution.

We have implemented this, to our knowledge for the first time in its general form, in the full-potential linear augmented plane wave (LAPW) method [11]. As a detailed description of this implementation will be given elsewhere we mention here just one important technical detail. In order to simplify the plane wave augmentation at the LAPW boundary, a spin independent LAPW basis set is constructed by defining the numerical augmentation functions inside the muffin-tin spheres as solutions to radial equations involving the nonmagnetic potentials v. Local orbitals [12] are included in the basis set, to more than compensate any potential loss in accuracy compared to having separate spin-up and spin-down functions as is usual for collinear magnetism.

In this work, where we are interested in the interplay of the two terms in Eq. (1) that involve Pauli matrices, we have chosen a system where both these terms are large. Among the actinides, for which the spin-orbit coupling is substantial, the simplest magnetic system is probably δ-Pu which forms in the fcc structure. Earlier calculations have shown that δ-Pu has a stable ferromagnetic solution at the experimental lattice constant, 8.75 a.u., with a large spin as well as orbital moment [13,14]. However, the temperatures for which this phase exists are far above any possible ordering temperature. In that sense this system might be viewed as primarily of pedagogical interest, although the possibility of epitaxial stabilization has not been fully explored.

Two self-consistent calculations, including all relativistic corrections up to spin orbit, have been performed at the experimental volume with the average magnetic moment pointing in the [001] and [111] directions, respectively. It is found that, among these two directions, the easy axis is along [111] since its total energy is 8 meV lower. This indicates that the [001] solution is not stable, but due to its high symmetry it is a stationary solution which permits a self-consistent solution. The spin moments are found to be $4.52\mu_B$/atom and $4.47\mu_B$/atom along [001] and [111], respectively, in good agreement with earlier calculations [14].

In addition to the magnetization density forming the moments there are also nonvanishing components perpendicular to it. In Fig. 1 three-dimensional isosurfaces of $m_x(\vec{r})$ and $m_y(\vec{r})$ are plotted for the case when the average moment points along z, i.e., [001]. The view is along the direction of the average moment and the densities are plotted in a cubic cell containing an atom and its 12 nearest neighbors. These components of the magnetization density have zero total magnetic moments when integrated over the unit cell as the positive and negative parts cancel each other. The magnetization density shows a rather complicated pattern, with several different lobes at each atom for different heights along the z axis. All atoms are equivalent by the translation symmetry and have the same magnetization density.

The maximum angle with which the total magnetization density points away from the [001] direction is 5°,

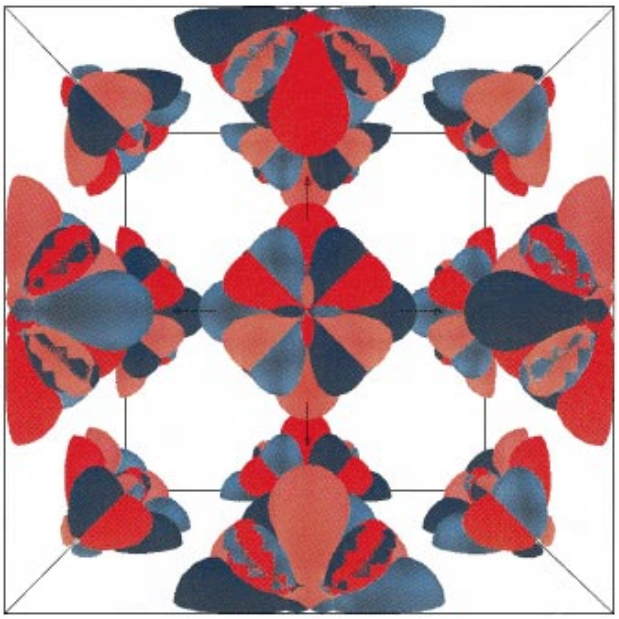

FIG. 1 (color). Three-dimensional isosurfaces of m_x (blue) and m_y (red), calculated when the average moment is along the [001] direction, are plotted within a cube, centered around an atom and going through its nearest neighbors, with the lengths of its sides equal to the fcc lattice constant. These isosurfaces correspond to positive (dark color) and negative (light color) densities of $10^{-3}\mu_B$/a.u.^{3}. In order to facilitate the understanding of this color code the actual direction of the magnetization density within the x-y plane is shown for four symmetrical points.

and although the part of the magnetization density, $\vec{m}_\perp$, which is perpendicular to the average spin moment has a zero moment, the moment obtained by integrating its magnitude $|\vec{m}_\perp|$ is $0.1\mu_B$/atom which is 2% of the integrated value for $|m_z|$.

It is rather easy to verify that the total magnetization density has tetragonal symmetry when treated as a vector quantity: For the central atom the NCM part of the magnetization density along the positive x axis, which is to the right in the figure, and slightly above the (001) plane going through its nucleus, is pointing mainly in positive x axis as seen by the dark blue lobe. When this density is rotated in a positive sense in steps of 90° around the z axis (directed out of the plane) going through the atom, it points successively in positive y (dark red), negative x (light blue), and negative y (light red) directions. In order to visualize this the direction of $\vec{m}_\perp$ is shown for four points in Fig. 1. The same rotational symmetry can also be observed for the four atoms in the foreground of the cube. Here it is also possible to see that there is a nodal (001) plane going through the nucleii of the atoms, situated at the edges of the cube, where the NCM part of the magnetization density is zero. The direction of the NCM part, i.e., the in-plane component $\vec{m}_\perp$, of the magnetization density is shown by arrows in Fig. 2 for a (001) slice slightly above the corresponding nodal plane for the central atom. From this figure it is possible to see how the magnetization direction varies continuously. The local point group symmetry of the atom from the calculated magnetization density is found to be isomorphic to C_{4h} [15], in contrast to the larger group D_{4h} for the case when the magnetization is strictly collinear along z. The two point groups differ in that the latter includes some mirror planes. Although the local symmetry should be the same for all fcc ferromagnets, the rather complicated form of the density in Fig. 1 is caused in part by the fact that this magnetization density is formed mainly by f orbitals.

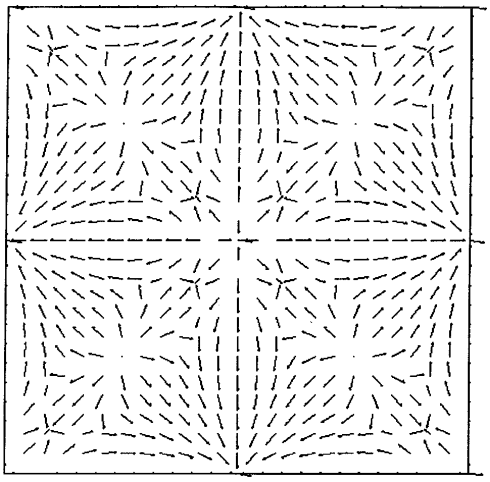

FIG. 2. The direction of the in-plane component of the magnetization density, i.e., the NCM part, is plotted for a (001) plane sliced $a/10$ above the center of the cube in Fig. 1, where a is the fcc lattice constant.

In Fig. 3 similar isosurfaces are plotted for the three components of the magnetization density pointing along $[1\bar{1}0]$, $[\bar{1}01]$, and $[01\bar{1}]$, when the average magnetization points along the [111] direction. The three components are all perpendicular to the average direction. The reason to plot these linearly dependent components and to view the plot from the [111] direction is to emphasize the local three fold rotational symmetry. Although this figure becomes more complicated with three components and hence six isosurfaces, the same conclusions may be drawn as for the [001] case: All these components average out to zero and they fulfill the threefold symmetry of the local point group, which is now isomorphic to C_{3i}. Again this point group differs from the one assuming collinear magnetization density, D_{3d}, by having less mirror planes.

These noncollinear densities originate from the spin mixing caused by the spin-orbit coupling term in Eq. (1). This leads to spinor solutions that cannot be rotated into a collinear solution, but produce a nontrivial $\vec{m}$ in Eq. (2). In the present case, the atoms are situated at symmetry sites with rotation axes and this noncollinearity averages out to a zero moment. The resulting noncollinear magnetization density produces a noncollinear exchange-correlation potential $\vec{b}$, which alters the final self-consistent solution. This general effect shows that the inclusion of spin-orbit coupling in a full-potential method actually, strictly speaking, requires the present NCM formalism. If the spin-orbit coupling term is neglected

FIG. 3 (color). Isosurfaces of the components of the magnetization density along $[1\bar{1}0]$ (blue), $[\bar{1}01]$ (red), and $[01\bar{1}]$ (green), calculated for the case of the average moment along the [111] direction are shown for the same cube as in Fig. 1 but viewed from the [111] direction. Both positive (darker colors) and negative (lighter colors) values are plotted, and the same isovalue is used as in Fig. 1.

in Eq. (1), spin mixing occurs only via the exchange-correlation potential and a truly collinear magnetization density can provide a stable solution.

As the intra-atomic NCM has to have zero moment in the presence of a rotation axis, it is also interesting to study cases when there is none. This is, for instance, the case if the magnetic moment is forced slightly off the [001] direction. Then the NCM moment is found not to cancel which, since this direction is unstable, leads to a further tipping away from the symmetry axis of the average moment, and finally ends with a self-consistent solution with the magnetic moment along an easy axis. So, in a sense, the NCM density of Fig. 1 is a precursor of the tipping of the magnetic moment and the canceled moment the indication that the solution is locally stationary.

Another interesting situation occurs in more complicated lattices, such as in the case of U_3P_4 where the U sites have no symmetry axes. Calculations for this system were recently reported [8] where it was found that the uranium magnetic moments tilt slightly off the [111] direction. Although that calculation did not allow for it, this can be understood in the present context as a noncancellation of the microscopic noncollinear moment for the [111] direction, leading to the self-consistent solution with a tilted moment. In that particular case, the effect is like the Dzialoshinski-Moriya mechanism [16], which was originally based upon similar symmetry arguments. A fundamental difference is that this is usually taken to be due to purely interatomic interactions of the form $\vec{D}_{ij} \cdot \vec{S}_i \times \vec{S}_j$, where $\vec{S}_i$ is the magnetic moment of atom i and $\vec{D}_{ij}$ is the coupling constant.

In summary, by means of general-LSDA calculations, a new kind of ground state solution has been obtained, manifested by a "microscopically" noncollinear magnetization density that changes direction on intra-atomic length scales. This is an effect which is caused by a general interplay between the local exchange responsible for the magnetization density and the spin-orbit coupling, and which is sensitive to the space group symmetry. Intra-atomic NCM has also recently been suggested to be present in the class of manganites that displays colossal magnetoresistance, [17] where the Mn d orbitals might not all have the same spin quantization axis. The spin-orbit induced effect is naturally smaller for the $3d$ transition metals than for Pu, but it is present and computationally observable in those cases too. It would be very interesting if this effect could be experimentally verified. This could maybe be accomplished either by direct detection of the NCM density, by means of, e.g., neutron scattering, or by probing the local symmetry of the magnetic atoms, with e.g., spectroscopic means.

Discussions with W. E. Pickett, P. Söderlind, and V. P. Antropov are thankfully acknowledged. This work has been supported by Office of Naval Research, and calculations have been performed at the NAVO Supercomputer Center of Department of Defense.

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