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Symmetry properties of intra-atomic spin and angular momentum densities: application to U_3Sb_4

K Knöpfle, L M Sandratskii and J Kübler

Institut für Festkörperphysik, Technische Hochschule, D-64289 Darmstadt, Germany

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Abstract. We consider the formation of the atomic spin and orbital moments in the framework of the local spin-density functional approximation by examining and exhibiting the symmetry properties of the intra-atomic spin and angular momentum densities, focusing on general principles, and elaborating by means of the realistic example of U_3Sb_4 which is a noncollinear ferromagnet. We expose the role of the symmetry properties in determining the intra-atomic noncollinearity of the spin and orbital moments, which we connect with the inter-atomic configurations of the atomic moments.

1. Introduction

The magnetic moment of an atom in a crystal is composed of two parts, one originating from the spin of the electrons, and the other from their orbital motion. In the magnetism of the 3d metals and compounds, the orbital moment plays a secondary role only, and can be treated as a small correction to the spin moment. The few exceptions where a peculiar compensation of the spin moments of different atoms leads to orbital moments being of primary importance (see, e.g., [1, 2]) rather confirm this statement than contradict it. With increasing atomic number of the constituent atoms, the spin-orbit coupling (SOC) grows, and, since SOC is closely connected with the formation of the orbital moment, this part of the magnetic moment gains importance for heavier systems. Thus, investigations of uranium compounds (see, e.g., [3–6, 8]) have shown that, in striking contrast to the case for 3d systems, the value of the orbital moment of the U atom usually exceeds the value of its spin moment.

Since the magnetic moments of various U compounds (see, e.g., [5, 6] and references therein) have been successfully calculated using the local density functional approximation (LDA) [7], we may assume that the LDA provides a solid theoretical basis. Yet, up to now, only the integrated atomic orbital moments have been obtained, and no attempt has been made to investigate their formation on the basis of intra-atomic angular momentum densities. With the present communication we want to contribute to filling this gap, and report calculations of the intra-atomic angular momentum densities.

Recent findings concerning the noncollinearity of the magnetic structure of a number of the U compounds [6, 8] provide a further incentive to examine the formation of magnetic moments. In particular, it was shown that for a broad class of U compounds a collinear arrangement of the atomic moments is improbable. We supplied [6, 8] symmetry arguments supporting this statement, and suggested addressing this phenomenon as *noncollinearity predetermined by symmetry*. This kind of magnetic structure possesses the additional

interesting feature of showing an inevitable noncollinearity of the spin and orbital moments residing on the same atom. This new type of magnetic noncollinearity has been detected in a number of theoretical studies [1, 6, 9, 10], and appears to be important for the explanation of the weak ferromagnetism of Mn_3Sn [1] as well as the magneto-optical properties of LaTO_3 [2]. In the present paper we show how this type of noncollinearity emerges from the properties of the spatial distribution of the corresponding intra-atomic densities.

The theory is applied to the ferromagnetic noncollinear compound U_3Sb_4 which, for our purposes, is convenient for the following reasons. First, we have recently [6] studied the integrated atomic magnetic characteristics of U_3Sb_4 which supplies a good basis for the present investigation. Second, the six U atoms in the unit cell of U_3Sb_4 separate into two groups of inequivalent atoms. This enables us to contrast and interpret the properties of the two groups in terms of features of the spin and angular momentum densities.

This communication is also motivated by the recent work of Nordström and Singh [11], who calculated the spin density in a collinear ferromagnetic state of Pu and found the density to be noncollinear. These authors use a full-potential method to treat the noncollinearity of the intra-atomic spin density (SD) self-consistently. In the closing part of the paper, Nordström and Singh commented on our calculation for the ferromagnet U_3P_4 [8], and argued that the noncollinearity of the magnetic structure obtained by us cannot be related to the properties of the spin density because of the atomic sphere approximation (ASA) used in our calculations. This comment, however, has no basis, as we show by supplying symmetry arguments and providing results of direct calculations.

2. Computational approach

An effective single-particle Hamiltonian has been written as a sum of three contributions [5, 6, 12]:

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_{sc} + \hat{\mathbf{H}}_{so} + \hat{\mathbf{H}}_{orb}. \quad (1)$$

Here the first part is the scalar-relativistic Hamiltonian of a noncollinear magnet given by

$$\hat{\mathbf{H}}_{sc} = \sum_{\nu} \mathbf{U}^{\dagger}(\theta_{\nu}, \phi_{\nu}) \begin{pmatrix} H_{sc}^{\nu\uparrow} & 0 \\ 0 & H_{sc}^{\nu\downarrow} \end{pmatrix} \mathbf{U}(\theta_{\nu}, \phi_{\nu}). \quad (2)$$

$\mathbf{U}(\theta_{\nu}, \phi_{\nu})$ is a standard spin- $\frac{1}{2}$ -rotation matrix transforming a global coordinate system into a local system of atom ν ; $H_{sc}^{\nu\uparrow}$ and $H_{sc}^{\nu\downarrow}$ are the standard atomic scalar-relativistic Hamiltonians (spin up, spin down) [13] in the local frame of reference for the atom at site ν . The potentials entering these Hamiltonians are as usual in the LDA obtained via functional derivatives as discussed in reference [14].

The second term of the Hamiltonian (1) includes the spin-orbit coupling, and can be written in the local coordinate system of the ν th atom as follows [8]:

$$\hat{\mathbf{H}}_{so} = \sum_{\alpha} M_{\nu\alpha} \sigma_{\nu\alpha} \hat{l}_{\nu\alpha}. \quad (3)$$

Here the subscript α labels the Cartesian coordinates, σ_{ν} is the vector of the Pauli spin matrices, and \hat{l}_{ν} is the angular momentum operator. The coefficients $M_{\alpha\nu}$ can be found in [5].

To simulate the second Hund's rule, we follow the work of Eriksson *et al* [15], and add to the Hamiltonian of the problem an effective orbital-field term $\hat{\mathbf{H}}_{orb}$. In the atomic sphere of the ν th atom, this term has been written as

$$\hat{\mathbf{H}}_{orb} = I_{orb} L_z \hat{l}_z. \quad (4)$$

Here L_z is the projection of the atomic orbital moment onto the local atomic z -axis. The parameter I_{orb} was taken to be equal 2.6 mRyd [15].

The Hamiltonian (1) is written within the ASA, i.e. the interstitial region is eliminated and all potentials entering equations (2) and (3) are assumed to be spherically symmetric within the atomic spheres. For the present discussion, the following feature of the ASA Hamiltonian (1) is of great importance: the direction of the spin magnetization is assumed to be constant for all points inside the atomic sphere and is parallel to the direction of the atomic spin moment.

Knowing the eigenfunctions of the Hamiltonian, we can determine the atomic spin moment by integrating the spin density

$$\mathbf{S}(\mathbf{r}) = \sum_{\substack{nk \in \\ \text{occ.} \\ \text{states}}} \psi_{nk}^\dagger(\mathbf{r}) \boldsymbol{\sigma} \psi_{nk}(\mathbf{r}) d\mathbf{r} \quad (5)$$

over the atomic sphere:

$$\mathbf{S}_v = \int_{\Omega_v} \mathbf{S}(\mathbf{r}) d\mathbf{r} \quad (6)$$

where $\psi_{nk}(\mathbf{r})$ are *spinor* eigenfunctions, and $\boldsymbol{\sigma}$ is the vector of the Pauli spin matrices.

Also, the atomic orbital moment of the v th atom can be calculated as an integral of the angular momentum density (AMD) of this atom:

$$\mathbf{L}_v(\mathbf{r}) = \text{Re} \left\{ \sum_{\substack{nk \in \\ \text{occ.} \\ \text{states}}} \psi_{nk}^\dagger(\mathbf{r}) \hat{\mathbf{l}}_v \psi_{nk}(\mathbf{r}) \right\} \quad (7)$$

over the atomic sphere.

3. Symmetry aspects

As we will see, the directions of the calculated spin and orbital moments are strongly influenced by the symmetry of the Hamiltonian (1). This symmetry is specified by the atomic positions \mathbf{a}_v and the directions of the atomic magnetic moments \mathbf{e}_v . Indeed, any symmetry operator of the type $\{\alpha_R | \mathbf{t}\}$ transforms the Hamiltonian as follows:

$$\hat{\mathbf{H}}(\mathbf{a}'_v, \mathbf{e}'_v) = \{\alpha_R | \mathbf{t}\} \hat{\mathbf{H}}(\mathbf{a}_v, \mathbf{e}_v) \{\alpha_R | \mathbf{t}\}^{-1} \quad (8)$$

where $\mathbf{a}'_v = \alpha_R \mathbf{a}_v + \mathbf{t}$, $\mathbf{e}'_v = \alpha_R \mathbf{e}_v$.

To determine the symmetry operations of the Hamiltonian, we must find those operations which commute with the Hamiltonian. As follows from equation (8), these are the operations of the space group which leave invariant both the crystal and magnetic structures.

For further considerations, it is important that the densities (5) and (7) which are calculated with the eigenstates of the ASA Hamiltonian (1) do not fulfil the ASA restrictions, but rather possess spatially varying directions within the atomic spheres. Note that in the calculation of the new directions of the spin and orbital atomic moments (see, e.g., (6)), the full intra-atomic noncollinearity of the densities (5) and (7) is taken into account, although, to calculate the atomic potentials entering the ASA Hamiltonian (1), the charge and spin densities are spherically averaged in each atomic sphere.

Thus, starting with the Hamiltonian specified in terms of the directions of the atomic moments only, we obtain the SD and AMD with the direction continuously varying within the atomic sphere. Therefore, the following question is to be answered here: does the

symmetry group of the ASA Hamiltonian supply an adequate tool for studying the properties of the calculated intra-atomic vector densities?

The answer to this question is in the affirmative. Indeed, the transformation properties of the eigenstates of the Hamiltonian reflect the symmetry of the Hamiltonian. As a result, the densities constructed on the basis of these states preserve the whole symmetry of the initial Hamiltonian. Hence, we reach the important conclusion that *the ASA to the Hamiltonian of the problem does not change the symmetry of the Hamiltonian*, and, therefore, is as suitable for the study of the symmetry properties of a noncollinear magnetic crystal as a full-potential scheme that does not approximate the form of the Hamiltonian.

Thus, independently of which of the two schemes, the ASA or the full-potential one, is used, the following restriction is imposed by a symmetry operation $\{\alpha|\mathbf{t}\}$ on the intra-atomic densities:

$$\xi_i(\alpha\mathbf{r}) = \alpha\xi_j(\mathbf{r}) \quad (9)$$

where the vector field $\xi_i(\mathbf{r})$ stands for the spin or angular momentum density of the i th atom defined within its atomic sphere (or muffin tin for the full-potential scheme), the vector \mathbf{r} is measured from the centre of the sphere, and the atoms i and j in equation (9) are connected by the following relation:

$$\{\alpha|\mathbf{t}\}\mathbf{a}_i = \alpha\mathbf{a}_i + \mathbf{t} = \mathbf{a}_j. \quad (10)$$

Note that in the case where \mathbf{a}_j coincides with \mathbf{a}_i or differs from it by a lattice translation, equation (9) supplies a restricting symmetry condition on the density of the particular atom i ; otherwise we obtain a relation between densities of different atoms i and j .

4. Numerical results

We now turn to an application of the theory to the compound U_3Sb_4 . Recently we have shown [6] that the magnetic structure of this compound cannot be collinear. Starting the calculation with all of the magnetic moments initially directed along the (001) axis, we find that the moments of four of the six atoms move in the iterations, and settle down forming a noncollinear cone structure, shown schematically in figure 1. Simultaneously, the moments of the other two atoms stay parallel to the (001) axis. An explanation of this behaviour has been given earlier [6, 8], and is based on the following statement: *any variation of the magnetic structure during the calculation must preserve the initial symmetry of the Kohn–Sham Hamiltonian*. This means, on the one hand, that if a deviation of the magnetic moments from the initial directions would lead to a perturbation of the invariance of the Hamiltonian with respect to at least one symmetry operation, this deviation cannot take place, while, on the other hand, if a deviation of the magnetic moments from the initial directions does not destroy any symmetry operation present, then there are no symmetry reasons for the initial magnetic configuration to be retained, and the magnetic moments will start to rotate, tending to assume the state of lowest total energy. In the last case, the probability of the minimum of the total energy being accidentally assumed by the collinear structure is negligibly small, and we deal with the case of noncollinearity of the magnetic structure which is predetermined by the symmetry of the problem. Below, we supply a ‘microscopic’ picture, and show how the behaviour of the atomic moments is determined by the properties of the corresponding intra-atomic densities.

To understand why the moments of atoms 1–4 deviate from the (001) axis, in contrast to the moments of atoms 5 and 6, we consider the symmetry group of the Hamiltonian (1) assuming that all of the U moments are initially directed along the (001) axis. The space

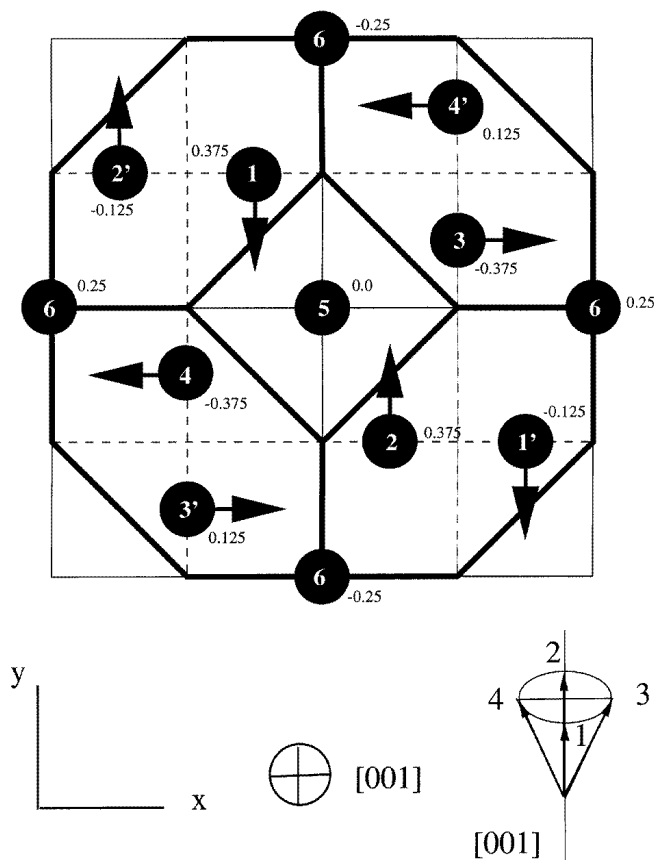


Figure 1. A projection of the atomic positions and atomic magnetic moments of U_3Sb_4 onto the xy -plane. Only the uranium atoms are shown. Atoms with the same number, whether or not they have a prime, are translationally invariant. Small numbers give the z -coordinates of the atomic positions. The projections in the bottom part of the figure show the deviation of the atomic magnetic moments of atoms 1–4 from the z -direction. The self-consistently determined angle of deviation of the atomic moments equals 7° [6]. The spin moment acquires the value of $1.90 \mu_B$ for atoms 1–4 and $1.99 \mu_B$ for atoms 5 and 6. The corresponding values of the orbital moment are -3.94 and $-4.18 \mu_B$. The calculated total magnitude of the atomic moment is in good agreement with the experimental estimate [16] of $2 \mu_B$. The horizontal distance between atoms 6 is the lattice constant $a = 17.2192a_0$ (a_0 is the Bohr radius). The radius of the U atomic spheres is $3.5a_0$.

group of the Hamiltonian contains in this case the fourfold symmetry operation $g_u = \{C_4I|0\}$, which is a combination of the rotation by 90° about the (001) axis passing through the position of atom 5 and the inversion. On being applied to the crystal, this symmetry operation keeps atom 5 at its position and moves atom 6 to a translationally equivalent position. Thus, according to equation (9), operation g_u imposes a symmetry restriction on the form of the angular momentum densities of the atoms 5 and 6. That is, assuming that the coordinate origin coincides with the centre of the atomic sphere, the densities at the points of the sphere with coordinates (x, y, z) , $(y, -x, -z)$, $(-x, -y, z)$, and $(-y, x, -z)$ will take the form (ξ_x, ξ_y, ξ_z) , $(-\xi_y, \xi_x, \xi_z)$, $(-\xi_x, -\xi_y, \xi_z)$, and $(\xi_y, -\xi_x, \xi_z)$. Here we take into account the fact that space inversion does not change the direction of the magnetic

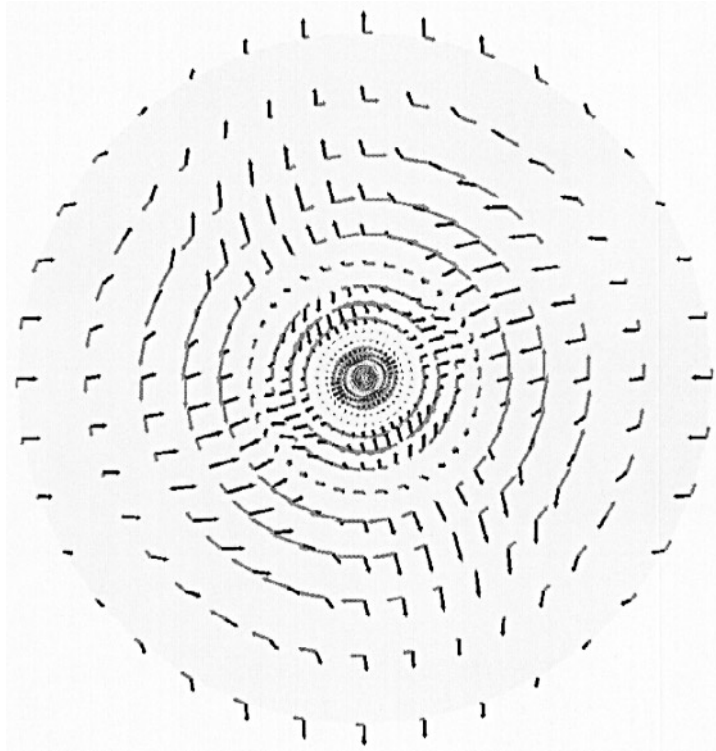


Figure 2. A cut of the xy -plane through the centre of atom 5. Black and grey arrows show the projections of the spin and angular momentum densities, respectively, onto the xy -plane. The scale for the arrows is 100 times that used in figures 4 and 5. The radius is $3.5a_0$, as in all subsequent figures.

moment, because of the axial nature of the vector. Evidently, integration over the atomic sphere leads in this case to cancellation of the x - and y -components of the density, and causes the atomic moments to appear parallel to the initial (001) direction.

In figure 2, we display a cut of the xy plane through the centre of atom 5, and show by arrows (in arbitrary units) the projections of the spin and angular momentum densities onto this plane. Both the varying direction of the densities, and the symmetry leading to the zero integrated values of the projections are clearly seen in the figure.

For atoms 1–4 the situation differs drastically. In this case the same symmetry operation g_u moves each atom to the position of another one. According to equation (9), the densities of atoms 1–4 are connected by a simple relation that guarantees the invariance of the crystal after the transformation. However, no symmetry restriction is imposed on the density of one particular atom. This means that there is no symmetry reason for the x - and y -components of the atomic moment to be zero. Therefore, the calculated magnetic moments deviate from the (001) direction and form a noncollinear magnetic structure.

Although we now understand the stability of the direction of the magnetic moment of atoms 5 and 6, and the inevitable deviation of the moments of atoms 1–4 from the direction of global magnetization, we notice that the picture is not yet complete, for the fourth-order symmetry operation g_u discussed above cannot explain the equivalence of atoms 5 and 6 obtained in the calculation. Also there is still no argument to explain why the moments of

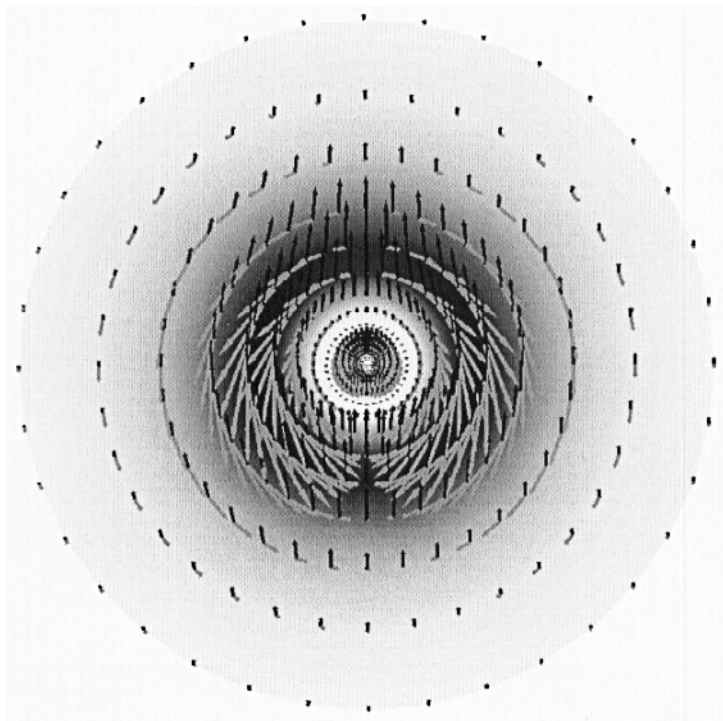


Figure 3. A cut of the xy -plane through the centre of atom 1. Black and grey arrows show the projections of the spin and angular momentum densities, respectively, onto the xy -plane. The intensity of the greyscaled background represents the length of the z -component of the spin density. The scale for the arrows is ten times that used in figures 4 and 5.

atoms 1–4 are parallel to the coordinate planes, xz or yz , as can be seen in figure 1.

To complete the description, the anti-unitary operation of time-reversal, K , must be taken into account. Evidently, a magnetic crystal cannot be invariant with respect to a pure time reversal, because this operation reverses the direction of any magnetic moment. However, time reversal can enter the symmetry group in combination with a unitary transformation. This happens in the case of U_3Sb_4 . The symmetry group contains four operations of such a type. For our purposes it is sufficient to consider one of them, since the other can be obtained by multiplication with the unitary operation g_u . The transformation $\{C_{2x} | (0 \frac{1}{2} \frac{1}{4})\} K$ is a symmetry operation of the initial collinear structure. Here C_{2x} is 180° rotation about the x -axis. This operation, first, transposes atoms 5 and 6, and determines their equivalence. Second, it keeps atoms 1 and 2 at their (or translationally equivalent) positions, and according to equation (9) imposes a symmetry restriction on the form of the intra-atomic densities of these atoms. A unitary rotation by 180° about the x -axis, accompanied by the time reversal, is equivalent to the reflection of the magnetization vectors in the yz -plane. Therefore, both the spin and angular momentum densities of atoms 1 and 2 have to be invariant under this transformation. Evidently, the integral of the density over the atomic volume results in this case in an atomic moment parallel to the yz -plane.

To illustrate how the anti-unitary operation influences the SD and AMD, we show in figures 3–5 cuts of three coordinate planes through the centre of atom 1. The symmetry with respect to the reflection in the yz -plane is clearly seen in the xy - and xz -cuts (figures 3

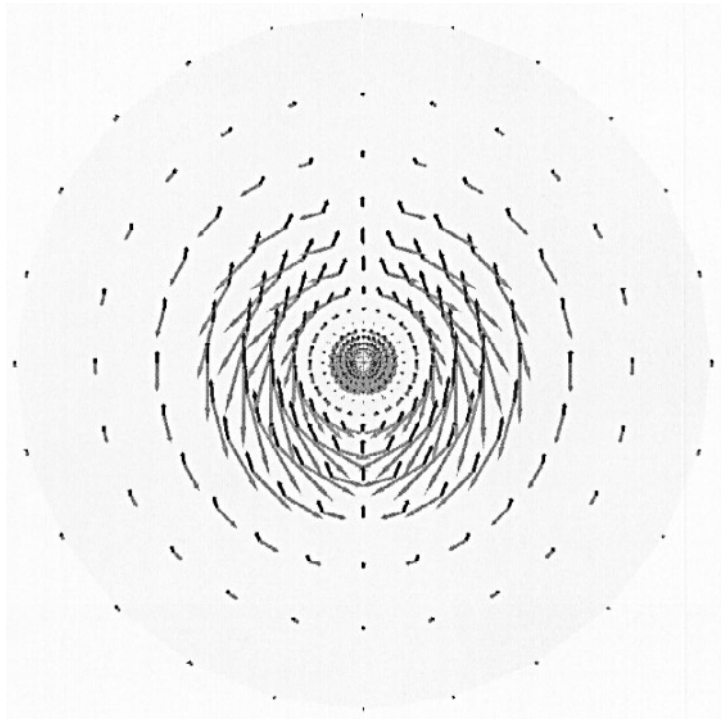


Figure 4. A cut of the xz -plane through the centre of atom 1. Black and grey arrows show the projections of the spin and angular momentum densities, respectively, onto the xz -plane.

and 4): there are uncompensated components of the spin and orbital moments along the y - and z -axes, in contrast to the zero integral value of the x -projection. The yz -plane (figure 5) shows no symmetry, and correspondingly no compensation of the components of the densities along the y - and z -axes.

Another important property of the SD and AMD that follows from the analysis of figures 2–5 is a mutual noncollinearity of the spin and angular momentum density vectors. The angle formed by two densities at a particular point cannot be determined without direct calculation, and is accidental from the point of view of symmetry. Since there is no symmetry operation that relates the directions of the two densities, this result can be treated as a necessary consequence of the symmetry of the problem. The mutual noncollinearity of two densities leads to the possibility of noncollinearity of the atomic spin and orbital moments. Indeed, integration of the SD and AMD of atom 1 results [6] in the noncollinearity of the spin and orbital moments of this atom.

In contrast to those of atom 1, the spin and orbital moments of atom 5 are collinear. This collinearity is directly related to the symmetry axis passing through atom 5: the symmetry properties of both densities result in the compensation of the components of the densities that are perpendicular to the (001) axis. Correspondingly, both the spin and the orbital moments of atom 5 are collinear with the (001) axis, and, therefore, with each other.

Thus, the spin and orbital moments of an atom in a crystal are collinear only in the case of an axial symmetry imposed on the intra-atomic SD and AMD. Conversely, in the absence of this symmetry, both intra-atomic noncollinearity of the spin and orbital moments of the same atom and intra-atomic noncollinearity of the moments of different atoms must

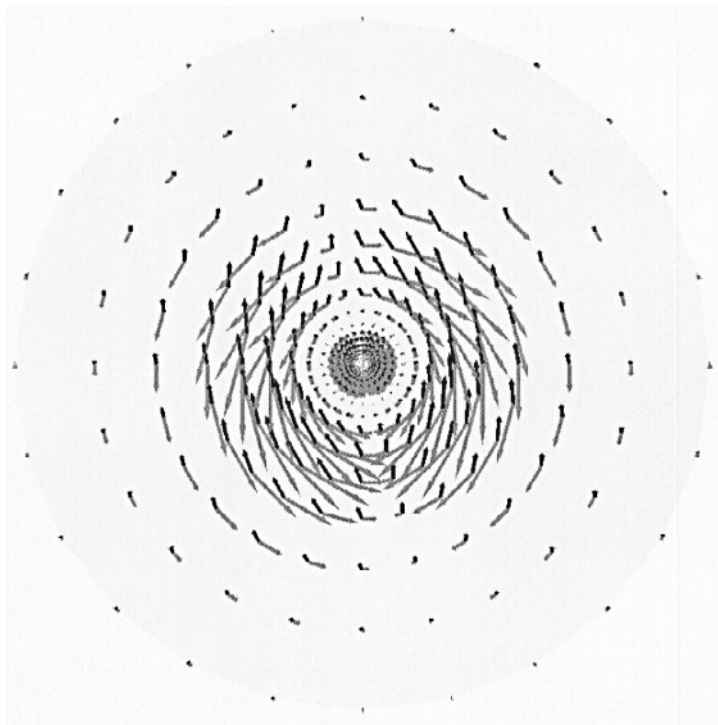


Figure 5. A cut of the yz -plane through the centre of atom 1. Black and grey arrows show the projections of the spin and angular momentum densities, respectively, onto the yz -plane.

appear.

Note that an isolated magnetic atom possesses the axial symmetry necessary for the collinearity of the atomic spin and orbital moments. It is the crystal environment that, under certain circumstances, leads to a loss of the axial symmetry, and consequently to noncollinearity. If, however, the strength of the intra-atomic spin–orbit coupling of the 5f electrons is stronger than the influence of the crystal environment, the disturbance of the axial symmetry will not be large. This is indeed the case for the U compounds, for we can see from figure 5 that the yz -plane through atom 1 is divided by the axis of the atomic moment into two almost mirror-invariant parts. Correspondingly, the angle between the atomic spin and orbital moments assumes only a small value of about 1° .

We finally want to comment briefly on the varying intensity of the background in figure 3. This intensity represents the magnitude of the z -component of the spin density at the corresponding point of the plane. The grey colour of the background is very intense for the ring area with the internal radius of about $0.8a_0$ and the external radius of about $1.6a_0$, where a_0 denotes the Bohr radius. (The radius of the atomic sphere is equal to $3.5a_0$.) The intensity decreases rapidly both in the direction of the centre and the direction of the border of the atom. An analysis of the calculated wave functions reveals (not surprisingly) that the most intense background corresponds to the spatial region of high 5f-electron density, thus confirming that the main contribution to the magnetic moments of the U atoms originates from the 5f electrons.

Summarizing, in the present paper we consider the formation of the atomic spin and orbital moments by studying the symmetry properties of the intra-atomic spin and angular

momentum densities, focusing on general principles, and elaborating by means of the realistic example of U_3Sb_4 which is a noncollinear ferromagnet. We expose the role of these properties in developing noncollinear magnetic configurations of atomic moments, as well as in the phenomenon of the intra-atomic noncollinearity of the spin and orbital moments.

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