Band-theoretical prediction of magnetic anisotropy in uranium monochalcogenides

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Magnetic anisotropy of uranium monochalcogenides, US, USe and UTe, is studied by means of fully-relativistic spin-polarized band structure calculations within the local spin-density approximation. It is found that the size of the magnetic anisotropy is fairly large (≈10 meV/unit formula), which is comparable with experiment. This strong anisotropy is discussed in view of a pseudo-gap formation, of which crucial ingredients are the exchange splitting of U 5f states and their hybridization with chalcogen p states (f–p hybridization). An anomalous trend in the anisotropy is found in the series (US ≫ USe < UTe) and interpreted in terms of competition between localization of the U 5f states and the f–p hybridization. It is the spin-orbit interaction on the chalcogen p states that plays an essential role in enlarging the strength of the f–p hybridization in UTe, leading to an anomalous systematic trend in the magnetic anisotropy.

71.20.Gj, 75.30.Gw, 75.50.Cc

Magnetic moments in solid originate in the spin and orbital components of electrons. Since electronic states responsible for the magnetism are normally localized in a particular atomic region, the moments can be regarded as site-selective quantities. Experimental techniques such as x-ray magnetic circular dichroism (XMCD) combined with the so-called spin and orbital sum rules [1,2] provide such separable information of the spin and orbital magnetic moments of ferro- and ferri-magnets. X-ray magnetic scattering [3] can also give us similar information.

Usually 5f electrons play major roles in magnetism of uranium compounds. Since the spin-orbit interaction (SOI) of the 5f electrons is relatively large, the size of the 5f orbital moment is often expected to be greater than the spin counterpart. Unlike the 4f orbitals in rare-earth element systems, the 5f states are more or less extended and may be possibly affected by their environmental effects, hybridization and crystal field. Thus, the magnetic moment in 5f systems must be strongly material-dependent. Magnetic anisotropy is another fundamental quantity in magnetism, which is often even more important for applications. However, the magnetic anisotropy energy is usually very small to be evaluated from first principles and furthermore its microscopic origins have never been clearly understood yet [4]. It is, therefore, quite interesting to study such issues on the magnetism by using a state-of-the-art band-theoretical technique.

Uranium monochalcogenides, US, USe and UTe, have NaCl-type cubic crystal structure and show a ferromagnetic order at the Curie temperatures, 177K, 160K and 104K, respectively [5]. It is well known that the monochalcogenides show strong magnetic anisotropy [6], where the [111] ([001]) direction is the easy (hard) axis. Interestingly, the saturation magnetic moment depends on the magnetization axis [7]. The largest moment along the easy axis, the smallest along the hard axis. The total magnetic moment per uranium atom increases from sulfide through telluride with increasing lattice constant. As long as the sulfide is concerned, the 5f electrons are considered to be itinerant from photoemission [8] and other experiments [9,10].

In the present study, mechanism of the magnetic anisotropy in the uranium monochalcogenides is investigated by first-principles calculations and an anomalous trend in the size of the anisotropy in the series is predicted. Our method is based on the local spin-density approximation (LSDA) to the density functional theory. One-electron Kohn-Sham equations are solved self-consistently by using an iterative scheme of the full-potential linear augmented plane wave method [11] in a scalar-relativistic fashion. We include SOI as the second variation every self-consistent-field step. The improved tetrahedron method proposed by Blöchl [12] is used for the Brillouin-zone integration. More details about our methods and calculated results are published elsewhere [13].

Figure 1 shows calculated fully-relativistic spin-polarized band structure of ferromagnetic US with the [111] magnetization. Shallow core U 6p states form \( j = 1/2 \) and 3/2 bands split by large SOI. S 3s bands are located just above the U 6p3/2 bands and have relatively large dispersion. S 3p bands are situated from 7 to 3 eV below the Fermi energy (\( \varepsilon_F \)). Dispersive bands appearing just below \( \varepsilon_F \) are made mostly of U d states. Relatively narrow U 5f bands are pinned around \( \varepsilon_F \). It is found that the largest contribution to the magnetic moments comes from U 5f states as expected. Calculated 5f moments of US are listed in Table I for three magnetization axes, [001], [110] and [111]. The spin moments hardly change with the magnetization axis while the orbital moments show large dependence of the axis. Consequently, the total moments depend strongly on the magnetization.
directions in Bohr magneton of US for different magnetization from the case of the [111] magnetization directions. Quantization axis for specifying j is taken as the same direction of magnetization. Let us discuss mechanism of the magnetic anisotropy and its relation to the magnetic moments.

Table I. Calculated 5f spin and orbital magnetic moments in Bohr magneton of US for different magnetization directions (\(\hat{M}\)). \(\Delta E\) is a difference in the total energy in meV from the case of the [111] magnetization.

| \(\hat{M}\) | spin | orbital | total | \(\Delta E\) |
|---|---|---|---|---|
| [001]\(^a\) | 1.61 | -2.13 | -0.52 | 14 |
| [110]\(^a\) | 1.60 | -2.24 | -0.64 | 5 |
| [111]\(^a\) | 1.60 | -2.33 | -0.73 | 0 |
| [111]\(^b\) | 1.3\(^c\) | -3.0\(^c\) | -1.7 | |

\(^a\)Present work.
\(^b\)Neutron-scattering experiment (Ref. [15]).
\(^c\)From analysis in Ref. [13].

axis, being in qualitatively good agreement with experiment [6]. Comparing with the experimental data, the spin moment is slightly overestimated while the orbital moment is underestimated. Origins of the discrepancy in the magnetic moments have been already discussed in the previous Hartree-Fock type study [17]. The total-energy difference shows that the [111] direction is the lowest while [001] is the highest. The difference of the total energy between the easy and hard axes is nothing but the magnetic anisotropy energy. The size of the magnetic anisotropy is comparable with experimental data [7] and is about 10\(^3\) times larger than that of 3d transition metals. Let us discuss mechanism of the magnetic anisotropy and its relation to the magnetic moments.

Because of large SOI of 5f electrons, \(j = 5/2\) and 7/2 states are roughly well separated and the occupied states are composed mostly of the \(j = 5/2\) states. The \(j_z\)-projected density of states (DOS) in the \(j = 5/2\) states is plotted in Fig. 2. One can easily note that a clear pseudo-gap is formed at \(\varepsilon_F\) in the [111] magnetization, while it becomes less apparent in the [001] direction. Relative stability of the [111] magnetization must come from the existence of the pseudo-gap.

In the case of [111], the plus and minus components are well separated. This is the exchange splitting of the bands and the pseudo-gap is considered to be a sort of the exchange gap. Only a small amount of mixing can be seen in the \(j_z = \pm 3/2\) states. On the other hand, the pseudo-gap is almost diminished in the case of [001] because of larger mixing in \(j_z = \pm 3/2\) and \(j_z = \pm 1/2\). By counting the number of occupied electrons in each partial DOS, one can get the occupation of each \(j_z\) state. For [111] \(\pm j_z\) state are well exchange-polarized but for [001] the occupations in the \(j_z = \pm 1/2\) bands are almost equal due to the mixing.

In order to get more intuitive insight into the occupations, a change-density plot of the 5f electrons around the U atom is depicted in Fig. 3. In the [111] magnetization, the 5f electrons tend to point to the direction of neighboring-U atoms; hexagonal brim stretching out in the (111) U plane and triangular bell around [111] direction are clearly formed. As a result, the 5f electrons have less distribution in the neighboring-S directions and they can reduce the hybridization with the S p states and gain the exchange splitting. The small mixing found in \(j_z = \pm 3/2\) can be understood by the fact that the \(j_z = \pm 3/2\) orbitals are extended to the S atoms with respect to the polar angle [18]. In the [001] magnetization, on the other hand, the 5f electrons again try to point to the U-U bonds, twelve [110] directions. In the \(xy\) plane gentle depression is formed in the nearest-
FIG. 1. Fully-relativistic spin-polarized band structure of ferromagnetic US with the [111] magnetization. The Fermi energy is chosen as the origin.

neighboring-S directions, because the $j_z = \pm 5/2$ states which spread in the $xy$ plane can prevent from mixing with the $S\,p$ states by using their azimuthal degrees of freedom. However, no depression is seen in the [00±1] directions. The $j_z = \pm 1/2$ states extending to the $z$ direction have no way to refuse the mixing with the $S\,p$ states because of less azimuthal degrees of freedom in its $m = 0$ component. This hybridization of the $j_z = \pm 1/2$ states with the neighboring $S\,p$ orbits destroys the pseudo-gap in the corresponding partial band and makes the [001] magnetization unfavorable \cite{19}. This is the most important mechanism of the magnetic anisotropy found in the present study and leads to a very interesting variation in the series of the uranium monochalcogenide as we shall discuss below.

A variation in the calculated spin and orbital magnetic moments for USe and UTe as well as for US is shown in Fig. 4. The spin and orbital moments increase as one goes from sulfide through telluride. This increase of the moments can be interpreted by narrowing of the U 5$f$ bands due to increase of the lattice constant. Based on such theoretical observation on the 5$f$-electron nature, we can expect a simple trend in the magnetic anisotropy. From sulfide to telluride, the lattice constant increases and the 5$f$ band width is reduced. Accordingly the magnetic moments are enhanced, approaching to an atomic limit. Therefore, the magnetic anisotropy may show a monotonic decrease from sulfide through telluride with increasing free-atom nature. But the reality is not so
simple and calculated magnetic anisotropy energy, plotted in Fig. 5, shows an anomalous behavior: decrease and increase with a minimum appearing at USe. Calling

that the strong magnetic anisotropy in the present compounds originates in the hybridization between the U 5f and chalcogen p states (f–p hybridization), differences in the chalcogen p states may be a clue to understand such an anomalous feature.

Hybridization depends upon spatial extension of the relevant orbitals via transfer integrals. Surprisingly, tails of the chalcogen p orbitals are almost the same if we consider the nearest neighbor distance between the U and chalcogen atoms. The Te 5p3/2 orbital has the longest tail of the chalcogens but the difference is not so large. In addition to the orbital extension, the orbital energy is another factor to determine the hybridization. Generally, the orbital-energy difference between the U 5f and chalcogen p states becomes smaller when going from sulfur through tellurium. Because of the large SOI, the Te 5p3/2 state raises up and its orbital-energy difference from the U 5f decreases substantially. Therefore, the f–p hybridization becomes very strong in the case of telluride. Basically, from sulfide through telluride, the U 5f electrons tend to be more localized due to enlargement of the lattice constant. But the f–p hybridization, which makes the [001] magnetization unfavorable, increases rapidly from selenide to telluride, resulting to large magnetic anisotropy in UTe. It should be noted that experimental data about the magnetic anisotropy have not been available for USe and UTe [20]. Experimental efforts to examine our prediction are strongly desired.

In conclusion, we have carried out fully-relativistic LSDA calculations for uranium monochalcogenides, US, USe and UTe. The magnetic anisotropy can be well described by the LSDA calculations. The pseudo-gap formation stabilizes the [111] magnetization. We have emphasized important roles of the $j_z = \pm 1/2$ states, which make the [001] magnetization unfavorable significantly. Calculated magnetic moments show the monotonic increase in the series with increasing lattice constant. On the other hand, the magnetic anisotropy shows the anomalous systematic trend. This can be understood by considering the hybridization of the U 5f states with the chalcogen p, especially the $p_{3/2}$ components. Anyhow, SOI not only on U but also on the chalcogen sites is essential to realize such interesting nature in magnetism of the uranium chalcogenides.

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![Fig. 5. Calculated magnetic anisotropy energy of US, USe and UTe, taken from the total-energy difference between the [111] and [001] magnetization directions.](image)

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