Experimental report

10/02/2017

Proposal: 5-51-516 **Council:** 4/2016

Title: Structure change and spin density distribution in unique magneticallylow-anisotropic compound U4Ru7Ge6

Research area: Physics

This proposal is a new proposal

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Samples: U4Ru7Ge6

Instrument	Requested days	Allocated days	From	To
D9	8	5	12/09/2016	17/09/2016
D3 High field >1T	5	9	20/06/2016	29/06/2016

Abstract:

U compounds usually exhibit huge magnetocrystalline anisotropy that is born in strong spin-orbit coupling in U ions and together with participation of 5f orbitals in anisotropic covalent bonding. Magnetization data measured on the U4Ru7Ge6 single crystal with ab initio electronic structure calculations reveal a rare exception from the rule. The easy magnetization direction of this cubic ferromagnet (Tc = 7.5 K) is [111] and the anisotropy field between [100] and [111] is ~ 0.2 T. At temperatures below Tc a rhombohedral distortion leading to 2 inequivalent U positions was observed by precise dilatometry and XRPD measurements. Appearance of the distortion is confirmed by the calculations which also predict for each inequivalent position a different U magnetic moment composed of mutually compensating spin and orbital components. Neutron diffraction experiments at D9 and D3 are proposed to address the important issues of physics of U4Ru7Ge6: the precise knowledge of crystal structure above and below Tc, respectively (D9) and details on the size of U magnetic moment at each inequivalent crystallographic position and the role of spin and orbital components (PND experiment at D3).

Introduction

$U_4Ru_7Ge_6$ is an itinerant ferromagnet with T_C = 10.7 K and spontaneous moment μ_s = 0.85 μ_B/f.u. at 1.9 K. Our magnetization measurements of a single crystal show, that it has the easy magnetization axis along the [111] direction at 1.9 K. It is a rare example of a uranium compound with low magnetic anisotropy with the magnetic anisotropy field of only ~ 0.3 T. DFT calculations incorporating spin-orbit coupling proposed lowering of the site symmetry at the U position. As the room temperature cubic structure (space group Im-3m) had only one U 8c site, it should split in the ground state to two sort of positions. One U 3b ion is predicted to have antiparallel spin and orbital component of almost the same magnitude leading to the magnetic moment close to zero. The remaining three U 9d sites have the uncompensated spin and orbital components leading to the non-zero magnetic moment of the whole unit cell. This symmetry change should consequently lead to a rhombohedral distortion of the originally cubic structure. Our thermal expansion measurements along [111] and [001] direction clearly shows, that this proposed effect is real as they exhibit different length change. However, the observed effect $\Delta L/L_{[111]}$is of the order of 10^{-6}. Thus it was not our task in performed neutron diffraction experiments to undoubtedly find the distorted ground state structure. We have checked the list of possible maximal subgroups and found that there is only one rhombohedral subgroup (space group R-3m). It satisfies both the manner of the thermal expansion data (where [001] direction expands, while [111] stays almost constant) and presence of the two different U sites as was proposed by DFT. For that reason we analyze our data comparably at the cubic Im-3m and rhombohedral R-3m space group.

Results

We have collected 370 inequivalent reflections (when assuming *R-3m* space group) with 0.1 $Å^{-1}$< sinθ/λ < 1.0 $Å^{-1}$ at 1.9 K and 20 K. One should notice, that our proposed small distortion does not cause appearance of any additional reflections. It only introduces different rules for merging of the equivalent ones and properly renames HKLs. As the intensities at 1.9 K (ordered state) should be affected both by nuclear and magnetic contribution we have measured the temperature dependence from 15 K down to 1.9 K of the four different strong reflections. Their intensity did not show any sign of change within the experimental error. Such observation is acceptable when the spontaneous magnetic moment of U4Ru7Ge6 is only 0.85 μB/f.u. It justifies the treatment of the intensities measured at 1.9 K as a purely nuclear ones and it also elucidates necessity of the polarized neutron diffraction experiment performed on D3. While analyzing the measured reflections we found out, that some of them are not in agreement with the others in the group of equivalent ones. Relative difference was up to 20 %. Further re-measuring of these inconsistent reflections lead to the improvement of the fit. Nevertheless we are not sure what instrumental effect caused such dramatic difference in measured intensities. Rietveld refinement of the D9 data (using re-measured reflections) with respect to both space groups (*Im-3m* and *R-3m*) resulted in similar agreement factors for datasets both above (20 K) and below (1.9 K) the ordering temperature. We have used anisotropic temperature factors and applied extinction corrections in our model. Possible site mixing was also checked with no significant effect on the agreement factors. As was expected, we were not able to clearly distinguish between the cubic Im-3m and rhombohedral R-3m space group. Nevertheless we obtained description of the structural and extinction parameters with respect to both structures. These are used as a reliable input for the refinement of the flipping ratios measured on D3.

Our sample was aligned to have external magnetic field parallel to the cubic $[111]_{cub}$ direction. Polarization of the incident beam was 0.95. We have collected set of the flipping ratios at the same temperatures (1.9 K and 20 K) as during the unpolarized experiment on D9 diffractometer. Applied magnetic field was 1 T and 9T, respectively. We have measured 238 flipping ratios up to $\sin\theta/\lambda = 0.7$ Å^{-1}. Obtained results were treated both with respect to cubic *Im-3m* and rhombohedral *R-3m* space group. While merging the equivalent flipping ratios within rhombohedral *R-3m* space group leads to the 53 independent values with internal agreement factor of 1%, the same approach for cubic *Im-3m* space group gives 32 independent values with much worse internal agreement factor of 3.5 %. It can be illustrated on the example of two reflections with dramatically different flipping ratios. These are namely $(0\ 3\ 0)_{hex}$ (labeled according to the *R-3m* space group in hexagonal representation) reflection with R = 1.28(2) and $(2\ 1\ 1)_{hex}$ with R = 0.79(2) as two inequivalent ones in the *R-3m* space group. But according to the *Im-3m* space group, they should be equivalent within the $(2\ -1\ 1)_{cub}$ family. It clearly shows, that cubic space group *Im-3m* cannot be used to describe the ground state of $U_4Ru_7Ge_6$. Thus we treated our data further only using the rhombohedral *R-3m* space group.

As the polarized neutron diffraction experiment on D3 diffractometer was performed prior to the structure determination on D9 we tried to analyze the flipping ratios with a structural input coming only from the room temperature XRPD data. Even from that rough approach we obtained results that are qualitatively in agreement with DFT calculations. Result of the following MAXENT method refinement is shown in Figure 1.

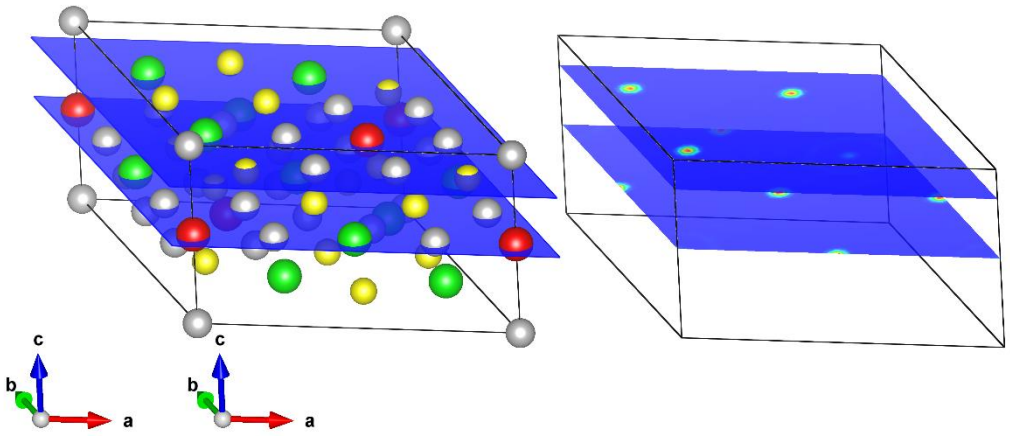

Figure 1 Spin density map as a result of the MAXENT method. Two cuts in the right panel clearly shows large positive spin density on the one set of U sites (marked green in the structural representation in the left panel) and almost zero density on the remaining fourth (red) U ion.

Precise refinement of the flipping ratios using the structural model from D9 data is in progress and will be summarized in the final report.