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Anomalous spin distribution in the superconducting ferromagnet UCoGe studied by polarized neutron diffraction

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We report a polarized neutron-diffraction study conducted to reveal the nature of the weak ferromagnetic moment in the superconducting ferromagnet UCoGe. We find that the ordered moment in the normal phase in low magnetic fields ($B\|c$) is predominantly located at the U atom and has a magnitude of $\sim 0.1\mu_B$ at 3 T, in agreement with bulk magnetization data. By increasing the magnetic field the U moment grows to $\sim 0.3\mu_B$ in 12 T and most remarkably, induces a substantial moment ($\sim 0.2\mu_B$) on the Co atom directed antiparallel to the U moment. The anomalous polarizability of the Co $3d$ orbitals is unique among uranium intermetallics and might reflect the proximity to a magnetic quantum critical point of UCoGe in zero field.

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Recently, UCoGe was identified as a member of the intriguing family of superconducting ferromagnets.[1] In these metallic ferromagnets superconductivity (SC) is realized well below the Curie temperature, T_C, without expelling magnetic order, and, even more peculiar, SC and ferromagnetism (FM) are carried by the same electrons. This is at odds with the standard BCS theory for phonon-mediated s-wave SC because the ferromagnetic exchange field is expected to inhibit spin-singlet Cooper pairing.[2] The unusual coexistence of SC and FM therefore calls for an alternative model: critical spin fluctuations near a magnetic instability provide the mechanism to pair the electrons in spin-triplet Cooper pairs. The superconducting ferromagnets discovered until now are UGe_2,[3] URhGe,[4] UIr,[5] and UCoGe.[1] FM in these metals has a strong itinerant character and consequently these metals can be tuned fairly easily by pressure or magnetic field to a magnetic quantum critical point and as such are excellent laboratory systems to investigate spin-fluctuation-mediated SC. Magnetically mediated SC is a central theme running through materials families as diverse as the heavy-fermion superconductors,[6] high-T_c cuprates and recently discovered FeAs-based superconductors.[7]

In UCoGe, weak itinerant ferromagnetism develops below the Curie temperature T_C=3 K.[1] Magnetization measurements on single crystals revealed a strong uniaxial magnetic anisotropy with a small ordered moment $m_0=0.07\mu_B$ directed along the orthorhombic c axis (see inset Fig. 1).[8] Muon-spin relaxation (μSR) experiments provide unambiguous proof for bulk magnetism, which coexists with SC below the superconducting transition temperature T_{SC}=0.5 K.[9]

In order to pinpoint the mechanism which gives rise to spin-fluctuation-mediated SC in superconducting ferromagnets a detailed understanding of the magnetic and electronic structure is essential. In this respect, the polarized neutron-diffraction (PND) technique is an extremely powerful tool as it gives direct information on the distribution of the magnetization in the unit cell and allows for the separation of the spin and orbital part of the magnetic moments.[10] PND experiments on UGe_2,[11] URhGe,[12] and URhSi (Ref. 13) (the latter compounds are isostructural to UCoGe), show that FM is due to itinerant uranium $5f$ electrons, and the magnetic-moment values are in good agreement with those derived by electronic structure calculations.[14,15] However, in the case of UCoGe the discrepancy between magnetization measurements[8] and calculations[16–18] is large. The calculations predict a small moment $\mu^U \sim 0.1\mu_B$ at the U site due to an almost complete cancellation of the orbital μ_L^U and spin μ_S^U magnetic moment. In addition, a much larger moment $\mu^{Co} \sim 0.2-0.5\mu_B$ is predicted at the Co atom. The magnetic moments on the U and Co sites are expected to orient parallel[16,18] or antiparallel[17] and consequently it is argued that the magnetic structure is quite complex and, for instance, magnetic stripe order[16] or an antiferromagnetic spin arrangement[17] have been proposed.

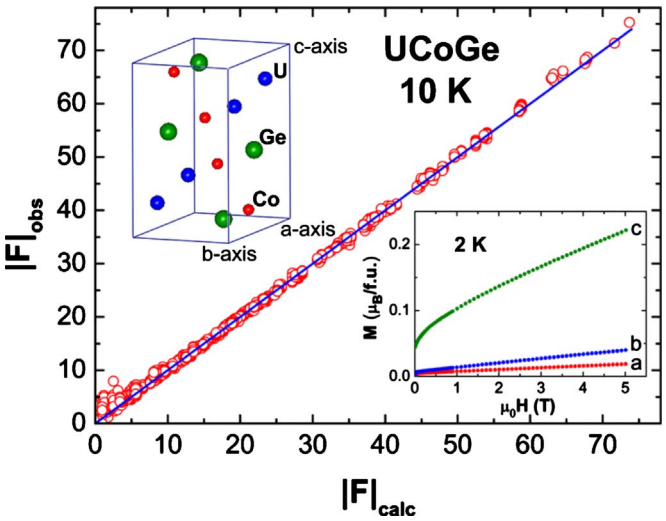

FIG. 1. (Color online) Observed versus calculated nuclear structure factors after correction for absorption and extinctions of the UCoGe single crystal in the unpolarized neutron-diffraction experiment at T=10 K. Upper inset: schematic representation of the TiNiSi structure adopted by UCoGe. Lower inset: magnetization versus magnetic field of UCoGe at T=2 K for a magnetic field applied along the three principal axes (Ref. 8).

In this Rapid Communication we report PND experiments on UCoGe conducted to identify the different contributions to the bulk magnetization in the normal phase [we apply a field $B\|c$ larger than the upper critical field $B_{c2}^{c}\simeq 0.5$ T (Ref. 8)]. We obtain a surprising result: in low magnetic fields the magnetization density is predominantly centered at the U atom, but in a large field (12 T) a substantial Co moment develops, which is directed antiparallel to the total U moment. The Co moment grows faster than the U moment. Such a high polarizability of the Co $3d$ orbitals is highly unusual[19] and reflects the proximity to a magnetic quantum critical point of UCoGe in zero field.

UCoGe crystallizes in the orthorhombic TiNiSi structure with space group *Pnma* (Ref. 20) (see inset Fig. 1). Neutron-diffraction experiments were carried out on a carefully heat treated single crystal,[21] prepared in a triarc furnace by the Czochralski technique. The sample was shaped into a bar along the b axis with dimensions $1\times 1\times 5$ mm^3. Resistivity measurements attest the high quality of the sample. The residual resistance ratio is 30, $T_C=2.8$ K and $T_{SC}=0.6$ K. Magnetization data taken for a field along the orthorhombic a, b, and c axes at $T=2$ K are shown in the lower inset of Fig. 1.[8] The bulk magnetic moment at $T=0.1$ K in 3 T and 12 T can be deduced by extrapolating the magnetization data for $B\|c$ and amounts to 0.17 μ_B/f.u. and 0.35 μ_B/f.u., respectively.

The nuclear structure parameters of the single crystal were determined at the D15 diffractometer installed at the Institute Laue-Langevin (ILL) with a wavelength of 1.17 Å in a four-circle geometry using a closed-cycle refrigerator. Absorption and extinction corrections were made. A large data set comprising of 1169 reflections was recorded at 10 K. The refinement of the structure with residual $R_w=1.2\%$ (see Fig. 1) yields lattice parameters $a=6.813$ Å, $b=4.203$ Å, and $c=7.215$ Å, and atomic coordinates close to those reported in Ref. 20.

In a neutron-diffraction experiment on a ferromagnet one typically measures the magnetic structure factor $F_M(\mathbf{Q})\propto\Sigma_j\mu_{j\perp}f_j(\mathbf{Q})e^{i\mathbf{Q}\cdot\mathbf{r_j}}$, where $\mu_{j\perp}$ is the component of the jth magnetic moment perpendicular to the scattering vector $\mathbf{Q}$ and $f_j(\mathbf{Q})$ is the magnetic form factor of the jth ion at position r_j in the unit cell. Using unpolarized neutrons one records an intensity proportional to the sum of $|F_M(\mathbf{Q})|^2$ and the nuclear structure factor squared $|F_N(\mathbf{Q})|^2\propto|\Sigma_j b_j e^{i\mathbf{Q}\cdot\mathbf{r_j}}|^2$. However, when the magnetic moment is small, as is the case for UCoGe, $|F_M(\mathbf{Q})|^2$ is too small compared to $|F_N(\mathbf{Q})|^2$ and cannot be determined precisely. A familiar way to improve the sensitivity is the use of polarized neutrons.[10] In the PND experiment one then measures the intensities $I^{\pm}(\mathbf{Q})\propto|F_N(\mathbf{Q})\pm F_M(\mathbf{Q})|^2$, where the + and − sign refer to up and down polarization directions of the incoming neutron beam. In practise one collects flipping ratios $R(\mathbf{Q})=I^{+}(\mathbf{Q})/I^{-}(\mathbf{Q})$ at many Bragg reflections. The precise knowledge of $F_N(\mathbf{Q})$ that is determined in the unpolarized experiment is crucial to evaluate $F_M(\mathbf{Q})$ and the magnitude of the magnetic moment.

The PND experiment was carried out at the D23 diffractometer at the ILL with the neutron beam polarized to 92%. The UCoGe single crystal was glued to the cold finger of a dilution refrigerator with the c axis vertical. Two data sets $R(\mathbf{Q})$ were collected at $T=0.1$ K in magnetic fields of 3 and 12 T applied along the easy direction for magnetization (c axis). Each data set consisted of typically 60 inequivalent reflections of the ($hk0$) and ($hk1$) type.

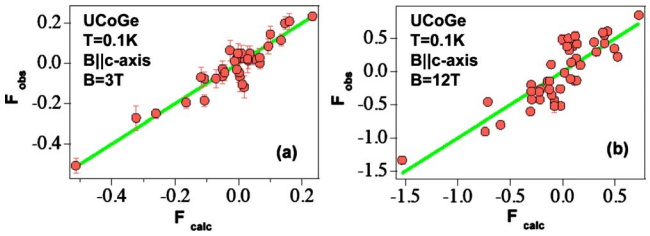

FIG. 2. (Color online) Observed versus calculated (solid line) magnetic structure factor of UCoGe for the polarized neutron-diffraction experiment at $T=0.1$ K in an applied field ($B\|c$) of (a) 3 T and (b) 12 T.

The uranium magnetic form factor is usually expressed within the dipolar approximation by the formula $f(\mathbf{Q})=\langle j_0(\mathbf{Q})\rangle+C_2\langle j_2(\mathbf{Q})\rangle$, where $C_2=\mu_L^{\mathrm{U}}/(\mu_S^{\mathrm{U}}+\mu_L^{\mathrm{U}})=\mu_L^{\mathrm{U}}/\mu^{\mathrm{U}}$ and j_i is the radial integral for the relevant U^{3+} or U^{4+} configuration.[22] An equivalent expression can be written down for the Co magnetic form factor. By assuming a magnetic moment on the U or Co site only, we could not obtain a good fit of the experimental data $F_M(\mathbf{Q})$. However, when we assume that the U and Co atoms both carry a magnetic moment the refinement of the magnetic structure (see Fig. 2) leads to a much better fit (χ^2 reduces by a factor of 2 and 3 for the 3 T and 12 T data, respectively). In modeling the form factor we took into account spin and orbital contributions on the U site but a spin-only contribution on the Co site. The fit results did not allow to resolve the uranium valency because the magnetic form factors of U^{3+} or U^{4+} are very similar. On the other hand, the parameter C_2 depends strongly on the ion state of uranium. The best fits yield the moment values listed in Table I. The spin and orbital moments on the U atoms are antiparallel to each other. Remarkably, we find a significant spin moment on the Co site, which is oriented parallel to μ_S^{U} but antiparallel to the total μ^{U}. The obtained values of C_2 are close to value calculated in the intermediate coupling scheme for the free U^{4+} ions. Obviously, the values of μ^{U} are smaller than the free ion values. This is in line with the itinerant nature of the $5f$ states in UCoGe.

Another elegant, powerful and independent treatment of the data is the method of maximum entropy.[23] This technique gives the most probable magnetization distribution map compatible with the measured structure factors and their experimental uncertainties. Compared to the usual Fourier synthesis it does not need any *a priori* assumptions concerning the unmeasured Fourier components, which reduces both the noise and truncation effects. At the same time no detailed atomic model is needed for the refinement. The basic input required is the space group, the lattice constants and the flipping ratio's together with the corresponding measured nuclear structure factors. The unit cell of UCoGe was divided into $64\times 64\times 64=262\,144$ cells, in which the magnetization is assumed to be constant. The reconstruction was started from a flat magnetization distribution with a total moment in the unit cell equal to the bulk magnetization measured experimentally. Our most important results are summa-

TABLE I. Magnetic-moment values of UCoGe determined from the magnetization, μ_{bulk}, compared to the moments extracted from the PND experiment by the analysis of the form factor, where the flipping ratios were fitted to a model allowing for both uranium μ^{U} and cobalt μ^{Co} magnetic moments, and by the integration of the spin-density maps obtained by a maximum-entropy method. The PND experiment was carried out at $T=0.1$ K in a magnetic field $B\|c$ of 3 and 12 T. We assumed the uranium moment to have both spin μ_S^U and orbital μ_L^U part, whereas the cobalt moment was assumed to have only a spin part. The parameter $C_2=\mu_L^U/\mu^U$ and $\mu_{int}=\mu_{bulk}-\mu^U-\mu^{Co}$, which is the magnetic moment not associated with a particular atomic position, are listed as well. All units are in μ_B.

Field (T)	Magnetization	Form factor						Maximum entropy		
	μ_{bulk}	μ_S^U	μ_L^U	μ^U	μ^{Co}	C_2	μ_{int}	μ^U	μ^{Co}	μ_{int}
3	0.17(1)	−0.05(2)	0.18(1)	0.13(1)	−0.043(7)	1.4(2)	0.08(2)	0.10(1)	0.00(1)	0.07(3)
12	0.35(1)	−0.17(9)	0.49(9)	0.32(7)	−0.27(3)	1.54(9)	0.30(10)	0.26(1)	−0.10(1)	0.19(3)

rized in Fig. 3, where we have plotted the resulting magnetization density obtained from the data collected at 3 T and 12 T ($B\|c$) projected on the a-b plane in panel (a) and (c), respectively. The projected crystal structure is plotted in panel (b). The density map obtained from the 3 T data set exhibits a clear, positive density around the uranium position, whereas the density around the Co position is very small. The 12 T map, however, is extraordinary: the density at the uranium site has more than doubled with respect to the 3 T value, but at the same time a strongly localized, negative density has appeared at the Co site. By integrating over three dimensions around the U and Co atomic positions we obtain moments μ^U and μ^{Co} as listed in Table I. The values of μ^U are in good agreement with the ones extracted from fitting the form factor while the values of μ^{Co} are about a factor 3 smaller.

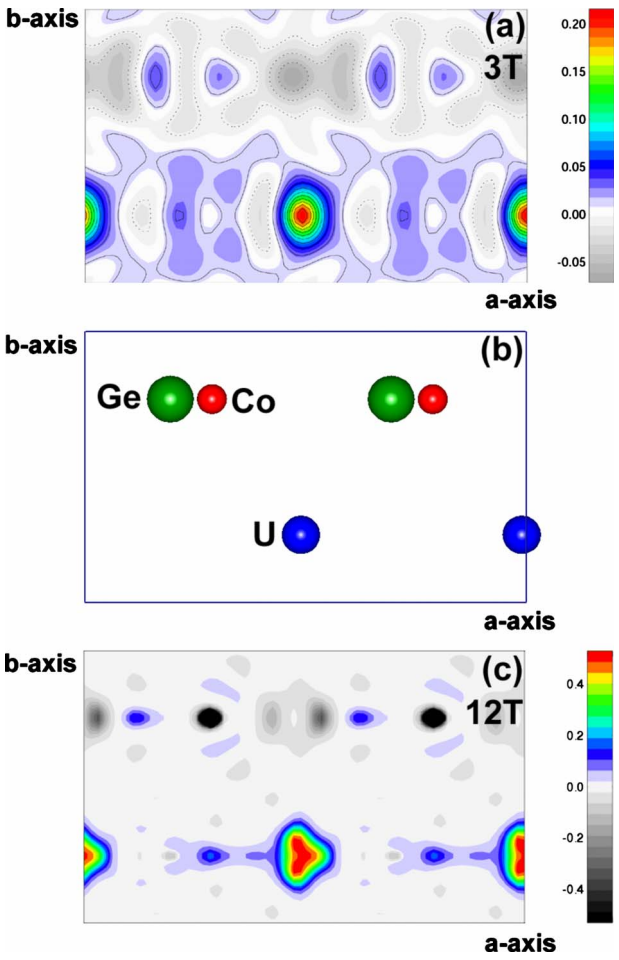

FIG. 3. (Color online) [(a) and (c)] Magnetization distribution of UCoGe obtained form maximum-entropy method projected onto the a-b plane measured in a field $B\|c$ of 3 T and 12 T, respectively, at $T=0.1$ K; (b) crystallographic unit cell projected onto the a-b plane. In all cases only half of the unit cell is projected. Notice the scales (in units μ_B Å^{-2}) differ in panels (a) and (c). In the lower panel the density at the Co position is off-scale and reaches −2.5 μ_B Å^{-2}.

We now have a detailed understanding of the magnetization density on a microscopic level and proceed to make several important conclusions. First, we conclude that the weak ferromagnetic state in UCoGe at low fields is predominantly carried by the U 5f moments. This is at variance with the electronic-structure calculations.[16–18] However, the PND data reveal that the Co moment is susceptible to a magnetic field, and magnetic moments on both the U and Co atoms, as predicted by the calculations, do occur in applied magnetic field. The small value of the Co moment in weak magnetic fields is in line with recent zero-field μSR (Ref. 9) and ^{59}Co nuclear quadrupole resonance[24] measurements. Second, in a magnetic field a moment μ^{Co} is induced on the Co site, oriented antiparallel to μ^U but parallel to μ_S^U. While the antiparallel orientation of the spin and orbital μ^U parts is common in 5 f systems,[25] the μ^{Co} moment is surprisingly large: at 12 T $|\mu^{Co}/\mu^U| \approx 0.4-0.8$, depending on the method of analysis. Thus in a large field $B\|c$ the spin arrangement in UCoGe is ferrimagnetic rather than ferromagnetic. Third, we conclude that both μ^U and μ^{Co} grow steadily with increasing $B\|c$. As expected, the magnetic field stabilizes ferromagnetic order and UCoGe is tuned away from the ferromagnetic instability. As a fourth important result, we find that the total magnetic moment $\mu^U+\mu^{Co}$ detected in the PND experiment is lower than the value deduced from the bulk magnetization. This indicates that the polarization of the interstitial regions and the contribution from the conduction electrons, which are neglected in the analysis of the PND data, play an important role in the magnetization process of UCoGe.

The results of our PND study allow us to draw a close parallel between UCoGe and URhGe: in low magnetic fields itinerant FM is predominantly due to the U 5f electrons but the magnetic interaction strength is different. This offers a unique opportunity to investigate spin-fluctuation-mediated SC in a systematic way. A recent step in this direction was

recently made by the extraordinary discovery of field-reentrant SC in UCoGe (Ref. 26) and URhGe.[27] Evidence has been presented that these exotic superconducting states are closely connected to the enhancement of spin-fluctuations associated with a spin-reorientation process which occurs in high magnetic fields $B\|b$.[26,28] As concerns UCoGe, for $B\|b$ the magnetization is linear in field and much smaller than for $B\|c$ (see Fig. 1) and we do not expect that a moment is induced on the Co site for this orientation.

Finally, we wish to stress the special role of the $5f$-$3d$ hybridization in UCoGe. In other magnetically ordered orthorhombic U *TX* compounds (where *T* is a transition metal and *X* is Si or Ge) no sizeable moments are found on the transition-metal atoms.[19] This indicates the strong polarizability of the Co $3d$ orbitals is directly related to the unique feature of UCoGe, namely, the proximity to a magnetic instability in zero field.[1] The application of a magnetic field drives the system away from the quantum critical point, which at the same time tends to stabilize μ^{U} and μ^{Co}. Induced magnetic moments on the transition-metal *T* atom have also been observed for magnetically ordered hexagonal U *TX* compounds, such as UCoAl.[29] Here the induced μ^{Co} is smaller and the ratio $|\mu^{\mathrm{Co}}/\mu^{\mathrm{U}}| \approx 0.2$ does not vary with the magnetic field.

In summary, we have conducted polarized neutron-diffraction experiments on a single crystal of the superconducting ferromagnet UCoGe for $B \geq B_{c2}\|c$ in order to solve the nature of the weak ferromagnetic state. The diffraction data are analyzed by two different methods: (i) fitting the data to a magnetic form-factor expression with moments on both the U and Co sites and (ii) by integrating the magnetization density maps produced by the maximum-entropy method. Both methods reveal that the weak ferromagnetic state in small applied magnetic fields is predominantly due to the U $5f$ moments. However, in a strong magnetic field a substantial moment on the Co atom is induced, antiparallel to the U moment, giving rise to a ferrimagnetic spin arrangement. The unusual polarizability of the Co $3d$ states points to a strong $5f$-$3d$ hybridization and might provide the key ingredient to understand the large anisotropy of the upper critical field B_{c2}.[8]

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