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 ($B \parallel c$) 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 new member of the intriguing family of superconducting ferromagnets. 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 pairings. 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$_2$, URhGe, UIr, and UCoGe. FM in these metals has a strong itinerant character and consequently it is argued that the magnetic structure is quite complex and, for instance, magnetic stripe order or an antiferromagnetic spin arrangement have been proposed.

In this Letter we report PND experiments on UCoGe conducted to identify the different contributions to the bulk magnetization in the normal phase (we apply a field $B \parallel c$ larger than the upper critical field $B_{c2}^{c} \simeq 0.5$ T) and Consequently it is argued that the magnetic structure is quite complex and for instance, magnetic stripe order or an antiferromagnetic spin arrangement have been proposed. UCoGe crystallizes in the orthorhombic TiNiSi structure with space group Pnma (see inset Fig. 1). Neutron diffraction experiments were carried out on a carefully heat treated single crystal, prepared in a tri-arc furnace.
by the Czochralski technique. The sample was shaped into a bar along the b axis with dimensions 1 \times 1 \times 5 \text{ mm}^3. Resistivity measurements attest the high quality of the sample. The residual resistance ratio is 30, \( T_C = 2.8 \text{ K} \) and \( T_{\text{sc}} = 0.6 \text{ K} \). Magnetization data taken for a field along the orthorhombic \( a \), \( b \) and \( c \) axis at \( T = 2 \text{ K} \) are shown in the lower inset of Fig. 1. The bulk magnetic moment at \( T = 0.1 \text{ K} \) in 3 T and 12 T can be deduced by extrapolating the magnetization data for \( B \parallel c \) and amounts to 0.17 \( \mu_B \text{/f.u.} \) and 0.35 \( \mu_B \text{/f.u.} \), 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 \( R_w = 12 \% \) yields lattice parameters \( a = 6.813 \text{ Å}, b = 4.203 \text{ Å} \) and \( c = 7.215 \text{ Å} \), and atomic coordinates close to those reported in Ref. 21.

In a neutron diffraction experiment on a ferromagnet one typically measures the magnetic structure factor \( F_M(Q) \propto \sum_j \mu_j \cdot f_j(Q) e^{iQ \cdot r_j} \), where \( \mu_j \) is the component of the \( j \)-th magnetic moment perpendicular to the scattering vector \( Q \) and \( f_j(Q) \) is the magnetic form factor of the \( j \)-th ion at position \( r_j \) in the unit cell. Using unpolarized neutrons one records an intensity proportional to the sum of \( |F_M(Q)|^2 \) and the nuclear structure factor squared \( |F_N(Q)|^2 \propto \sum_b b_l e^{iQ \cdot r_b} |^2 \). However, when the magnetic moment is small, as is the case for UCoGe, \( |F_M(Q)|^2 \) is too small compared to \( |F_N(Q)|^2 \) and cannot be determined precisely. A familiar way to improve the sensitivity is the use of polarized neutrons22. In the PND experiment one then measures the intensities \( I^\pm(Q) \propto |F_N(Q) \pm F_M(Q)|^2 \), where the + and − sign refer to up and down polarization directions of the incoming neutron beam. In practise one collects flipping ratios \( R(Q) = I^+(Q)/I^-(Q) \) at many Bragg reflections. The precise knowledge of \( F_N(Q) \) that is determined in the unpolarized experiment is crucial to evaluate \( F_M(Q) \) 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 \( R(Q) \) were collected at \( T = 0.1 \text{ K} \) in magnetic fields of 3 T and 12 T along the easy direction for magnetization (\( c \) axis). Each data set consisted of typically 60 inequivalent reflections of the (hk0) and (hkl) type.

The uranium magnetic form factor is usually expressed within the dipolar approximation by the formula \( f(Q) = \langle j_0(Q) \rangle + C_2 \langle j_2(Q) \rangle \), where \( C_2 = \mu_L^U / (\mu_L^U + \mu_L^S) = \mu_L^U / \mu_U^L \) and \( j_i \) is the radial integral for the relevant U\(^{3+}\) or U\(^{4+}\) configuration. 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 \( F_M(Q) \). 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 (\( \chi^2 \) reduces by a factor of two and three for the 3 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 1. 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 \( \mu_S \), but antiparallel to the total \( \mu_U \). 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 \( \mu_U \) 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

![FIG. 1: (Color online) Observed versus calculated (solid line) magnetic structure factor of UCoGe for the polarized neutron diffraction experiment at \( T = 0.1 \text{ K} \) in an applied field (\( B \parallel c \)) of 3 T (a) and 12 T (b).](Image)

![FIG. 2: (Color online) Observed versus calculated (solid line) magnetic structure factor of UCoGe for the polarized neutron diffraction experiment at \( T = 0.1 \text{ K} \) in an applied field (\( B \parallel c \)) of 3 T (a) and 12 T (b).](Image)
of the data is the method of maximum entropy. 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 ratios together with the corresponding measured nuclear structure factors. The unit cell of UCoGe was divided into $64 \times 64 \times 64 = 262144$ 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 summarized in Fig. 3 where we have plotted the resulting magnetization density obtained from the data collected at $3 \, \text{T}$ and $12 \, \text{T}$ ($B \parallel c$) 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 $3 \, \text{T}$ data set exhibits a clear, positive density around the uranium position, whereas the density around the Co position is very small. The $12 \, \text{T}$ map, however, is extraordinarily: the density at the uranium site has more than doubled with respect to the $3 \, \text{T}$ 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 $\mu^U$ and $\mu^{Co}$ as listed in Table 1. The values of $\mu^U$ are in good agreement with the ones extracted from fitting the form factor, while the values of $\mu^{Co}$ are about a factor 3 smaller.

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. 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 muon spin relaxation ($\mu$SR) and $^{59}\text{Co}$ Nuclear Quadrupole Resonance (NQR) measurements. Secondly, in a magnetic field a moment $\mu^{Co}$ is induced on the Co site, oriented antiparallel to $\mu^U$ but parallel to $\mu^U$. While the antiparallel orientation of the spin and orbital $\mu^U$ parts is common in $5f$ systems, the $\mu^{Co}$ moment is surprisingly large: at $12 \, \text{T}$ $|\mu^{Co}/\mu^U| \approx 0.4-0.8$, depending on the method of analysis. Thus in a large field $B \parallel c$ the spin arrangement in UCoGe is ferrimagnetic rather than ferromagnetic. Thirdly, we conclude that both $\mu^U$ and $\mu^{Co}$ grow steadily with increasing $B \parallel c$. 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 first step in this direction was recently made by the extraordinary discovery of field-reentrant SC in UCoGe and URhGe. 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 $B \parallel k_{Z抚}$. As concerns UCoGe, for $B \parallel b$ the magnetization is linear in field and much smaller than for $B \parallel c$, 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 UTX compounds (where $T$ is a transition metal and $X$ is Si or Ge) no sizeable moments are found on the transition metal atoms. 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. The application of a magnetic field drives the system away from...
the quantum critical point, which at the same time tends to stabilize $\mu^{U}$ and $\mu^{Co}$. Induced magnetic moments on the transition metal T atom have also been observed for magnetically ordered hexagonal UTX compounds, like UCoAl. Here the induced $\mu^{Co}$ is smaller and the ratio $|\mu^{Co}/\mu^{D}| \approx 0.2$ 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 magnetic state in small applied magnetic fields is predominantly due to the U 5$f$ 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 3$d$ states points to a strong 5$f$-3$d$ hybridization and might provide the key ingredient to understand the large anisotropy of the upper critical field $B_{c2}$.

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TABLE I: Magnetic moment values of UCoGe determined from the magnetization, $\mu_{\text{bulk}}$, 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 $\mu^U$ and cobalt $\mu^C$ 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 $B \parallel c$ of 3 T and 12 T. We assumed the uranium moment to have both spin $\mu^U_S$ and orbital $\mu^U_L$ part, whereas the cobalt moment was assumed to have only a spin part. The parameter $C_2 = \mu^U_L / \mu^U$ and $\mu_{\text{int}} = \mu_{\text{bulk}} - \mu^U - \mu^C$, which is the magnetic moment not associated with a particular atomic position, are listed as well. All units are $\mu_B$.

| Field | $\mu_{\text{bulk}}$ | $\mu^U_S$ | $\mu^U_L$ | $\mu^C$ | $\mu^C_{\text{int}}$ | $C_2$ | $\mu_{\text{int}}$ | $\mu^U$ | $\mu^C$ | $\mu_{\text{int}}$ |
|-------|---------------------|----------|----------|---------|---------------------|------|-------------------|--------|--------|------------------|
| 3 T   | 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 T  | 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)        |