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The magnetic structure of UIn_3: PAC on a polycrystal

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Abstract. PAC measurements on UIn_3 show that the U moments are oriented mainly along [001] in an AFII type ordering. A small scale deviation from this ordering must be present, for which two possibilities are proposed. There are several indications that on top of this small scale deviation another not yet understood perturbative effect occurs.

1. Introduction

$AuCu_3$ compounds of the type FX_3 with F a 4f or 5f element and X = In or Sn are known to show a variety of magnetic structures [1, 2]. For some of these materials—e.g. UIn_3—a final model for the magnetic order has not yet been found. From neutron diffraction measurements in the early seventies on a polycrystal of UIn_3 [2] the magnetic unit cell appeared to be doubled in all directions, resulting in a type II antiferromagnet (AFII) below a Néel temperature of 95 K (figure 1(a)). Due to the polycrystallinity of the sample, the absolute orientation of the opposite moments could not be determined. In the AFII structure no net magnetic field exists at the In position, as the contributions from neighbouring U atoms cancel pairwise. Several independent ^{119}Sn Mössbauer measurements in the early nineties [3–6] contradicted this simple structure: the ^{119}Sn probes occupying an In position do feel a small magnetic hyperfine field. Apparently a modification of the AFII structure is needed, to which the neutron diffraction was not sensitive. However, the interpretations from the different Mössbauer studies do not agree. Due to the higher sensitivity of the perturbed angular correlation (PAC) probe ^{111}Cd to magnetic and electric hyperfine fields, a PAC study may clarify the magnetic structure.

2. Experimental details

In a PAC experiment a trace quantity of radioactive nuclei is introduced into the sample. In our experiments we used ^{111}In which decays with a half-life of 2.83 days to an excited state of ^{111}Cd. The nuclear spins in the latter state form an unoriented ensemble. Out of this, an oriented subensemble is selected by observation of the emission direction of the first γ-ray from a $\gamma\gamma$-cascade in the further decay of ^{111}Cd. By emitting this γ-radiation, the

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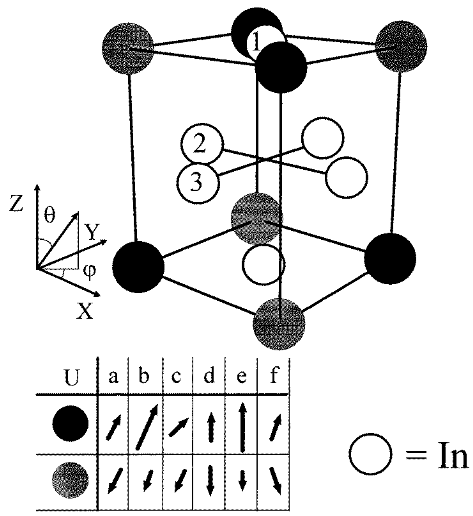


Figure 1. 1/8 of the AFII magnetic unit cell for UIn_3. White spheres are In, dark and grey spheres are U with antiparallel moments. The three inequivalent In positions are numbered. The inset illustrates small modifications to AFII. (a) Pure AFII, no direction specified (general case), (b) moments antiparallel but not equal in magnitude, (c) moments equal in magnitude but not perfectly antiparallel, (d)–(f) same as (a)–(c) but now with the orientation mainly along [001]. The polar angles (θ, φ) shown in the inset give the orientation of the local magnetic hyperfine field (note: not of the U moments) at any In position with respect to a natural axis system attached to the crystal structure. As in both models we propose the hff at all three positions has the same absolute orientation, one set of polar angles is indeed sufficient.

^{111}Cd nucleus enters a $5/2^+$ level with a half-life of 85 ns. During the lifetime of this state, the orientation of the subensemble changes ('precesses') due to interaction of the nuclear moments with the surrounding extranuclear fields. The decay out of the intermediate level is signalled by detection of the second γ-ray. As this detection is done with time and spatial sensitivity, the time evolution of the orientation of the subensemble can be reconstructed. After getting rid of the exponential decay stemming from the lifetime of the intermediate level, the so-called $R(t)$ function (e.g. figure 2) is obtained. The $R(t)$ function shows the time evolution of the nuclear spin orientation, and contains information about the strength, asymmetry and orientation of the perturbing extranuclear fields. These quantities are very sensitive to the electronic surroundings of the probe nucleus. Details about the perturbed angular correlation technique can be found in [7] and [8].

The ^{111}In atoms were brought into the sample by thermal diffusion at 500 °C for 24 h under vacuum. By this procedure 82% of the probes were found to populate the UIn_3 matrix; the remaining part was located in an In-rich near surface region. The latter part could be fitted in our data as a fraction with an electric field gradient close to the value known for pure In, with a broad distribution. The samples are very sensitive to corrosion by oxygen and moisture. At all stages of the measurement they were kept under an Ar atmosphere or under protecting glue. After the heat treatment the samples appeared to be broken into small splinters, probably due to internal stress. This had no influence on the local structure, as the measured hyperfine interaction parameters in the paramagnetic region are exactly as expected from our previous measurements in the $U(In_{1-x}Sn_x)_3$ system [9]. The dc magnetic susceptibility measurements were performed in the temperature range 4.5–200 K in magnetic fields up to 0.1 T using a Quantum Design MPMS-5 SQUID magnetometer.

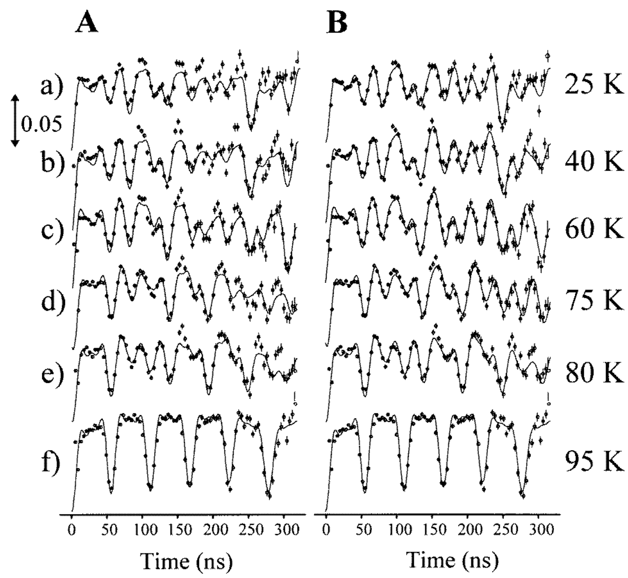
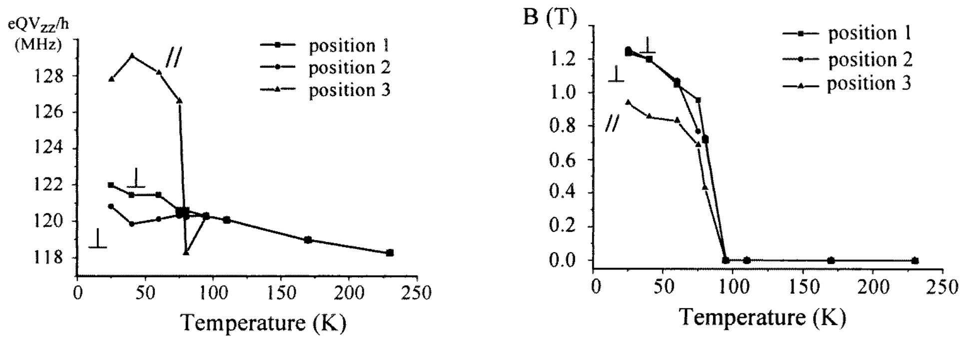


Figure 2. Spectra from 25 K to 95 K. (A) Fitted with three completely equal efgs and magnetic hffs, except for the angle β_i between them. (B) Different magnitudes for the three situations allowed.

3. Results and discussion

At room temperature and down to 95 K we observe an $R(t)$ function typical of a unique, axially symmetric electric field gradient (efg) (figure 2(f)). Its magnitude V_{zz} is directly related to the observed precession frequency $\nu = eQV_{zz}/h$, which is equal 117.1 MHz at 300 K. As the parent nucleus is ^{111}In, we expect the probes to occupy the In site (labelled 1–3 in figure 1). The point group of this site is $4/mmm$, which has indeed axial symmetry. The point group of the U site ($m3m$) has cubic symmetry, which would result in a zero efg and hence a constant $R(t)$. At interstitial sites in general no axial symmetry is expected. Therefore we can conclude that the ^{111}Cd probe indeed occupies exclusively the In position, as did ^{119}Sn in Mössbauer experiments. Due to crystal symmetry, the principal component V_{zz} of this efg is oriented along the normal to the face of the cube containing the considered In position (see also figure 5). While lowering the temperature, the efg increases linearly at a rate of $(137.3 \pm 0.3)\ 10^{-4}$ MHz K^{-1}, a typical behaviour for materials containing f elements [10, 11] (figure 3(a)). Between 95 K and 80 K, the $R(t)$-function becomes complex due to the appearance of a magnetic hyperfine field (hff) (figure 2). A consequence is that the three In sites in figure 1 are not necessarily equivalent any more: if we define a β_i which is the angle between the local hff and the principal component V_{zz} of the local efg at the ith In site, then these β_i are not necessarily the same for all three In sites. The relative orientation of the hff with respect to the efg is the principal criteria for hyperfine interaction methods to derive information on the magnetic structure. For instance, two possible antiferromagnetic configurations which may result in an hff, at least at some of the In sites, are either antiferromagnetically coupled ferromagnetic layers stacked in the [001]-direction with moments along [010] (call this case 1) or an NdZn structure [4, 5, 12] with moments pointing in the [111]-directions (case 2). In case 1 there is no hff at two-thirds of the In sites due to pairwise cancellation of the neighbouring moments, hence β_2 and β_3

have no meaning. At the remaining one-third of the sites, efg and hff are perpendicular ($\beta_1 = 90°$). In case 2 at all In sites the hff is parallel to the efg ($\beta_1 = \beta_2 = \beta_3 = 0°$). Three independent Mössbauer studies of UIn_3 by Krylov *et al* [3], Yuen *et al* [4, 5] and Begum *et al* [6] detected a small hff of about 1 T, contradicting this way the simple AFII structure proposed from neutron diffraction measurements [2]. In the analysis of Krylov, efg and hff are perpendicular for two-thirds of the probe sites. At the remaining one-third only an efg is present. No simple spin structure can explain this. Yuen found an hff at all sites, parallel to the efg. The model described above as case 2 would yield such a situation. In the paper by Begum some probes feel a combined efg and hff, while others feel only an efg. No further quantitative information is given, but this analysis resembles mostly that of Krylov.



(a) (b)

Figure 3. (a) Temperature dependence of the efg at the three inequivalent In positions when fitted as in figure 2(B). The symbols ⊥ and ∥ refer to the relative orientation between hff and efg. Both perpendicular sites behave practically in the same way. (b) Temperature dependence of the magnetic hffs corresponding to (a).

PAC measurements were carried out in an attempt to clarify these contradicting interpretations. First, we can rule out the parallel model (case 2) from [4] and [5]: without any discussion, a fit with all $\beta_i = 0°$ does not go through our data. Also the model from case 1 appears not to be possible, as all our probes do feel a non-zero hff. This and the fact that the measured hff is particularly small (about 1 T) makes it very likely that a small distortion of the originally proposed AFII structure will be a good solution to the data. Therefore we examined a broad class of small modifications to the situation of figure 1(a). Two types of modification with respect to the general case in e.g. figure 1(a) are possible: changing the magnitude of the oppositely directed moments (figure 1(b)) or changing their direction (figure 1(c)). Any of these modifications results in a net magnetic hff at the In position, which has the same absolute orientation for all three sites. The latter can be easily understood by considering that the magnetic hff at an In position results from the vector sum of the neighbouring U moments, and these neighbouring vectors are the same for any In site. The relative orientation of the efg with respect to the hff—as given by the angles β_i—is the only parameter which can be different from site to site. Hence, by examining all possible absolute orientations of the local magnetic hff, we do scan all possible modifications to an AFII type where the up and down moments from figure 1(a) are more or less antiparallel (the parallel model from [4] and [5] clearly does not belong to this class). Due to the crystal symmetry, it is not necessary to consider all possible absolute orientations, but only those where the polar angles θ and φ relative to the [001]-direction (figure 1) are both between 0° and 45°. For all these orientations a theoretical curve is fitted through the data at 40 K, allowing only the magnitude of the efg and the magnetic hff and their respective Gaussian distributions to vary. All these quantities are requested to be the same for the three sites. The χ^2-surface (figure 4) shows a clear minimum near $\theta = 0°$ (where φ is of no importance). This means $\beta_1 = 0°$ (parallel site, $\|$) and $\beta_2 = \beta_3 = 90°$ (perpendicular sites, $\perp$). Applying this model to other temperatures gives a reasonable fit (figure 2(A)), however with some significant deviations. Such a spin structure is consistent with the absence of a magnetic field at the centre of the cubic unit cell, as detected by μSR [13] (but see also below).

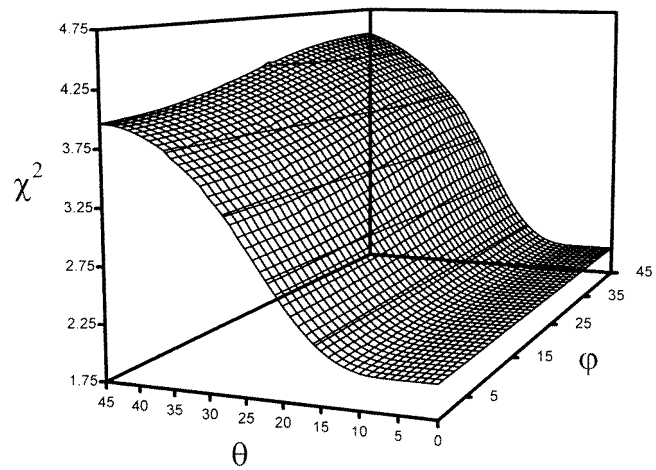


Figure 4. χ^2-surface for a fit at 40 K as a function of θ and φ. θ and φ define the orientation of the hff at position 1 with respect to the crystal and hence fix β_1. The hffs at positions 2 and 3 have the same absolute orientation but another β. This plot contains the χ^2 of 2116 fits; no smoothing is applied.

Before dealing with the deviations, we link the orientation of the local fields to the U moments. PAC is sensitive to the resulting fields at the probe's position, but only indirectly sensitive to the surrounding moments yielding these fields. Often more than one type of magnetic structure is able to yield the same local fields. Also here there are two possibilities to generate the measured β_i: making one of the two U moments larger than the other (figure 1(e) and 5(a)) or tilting them over an opposite small angle in the [010]-plane (figure 1(f) and 5(b)). But in both situations the U moments must be oriented almost along the [001]-axis. The latter is information which could not be obtained from neutron diffraction on a polycrystal.

The deviations in figure 2(A) indicate that we have not yet reached the final model. The fits of figure 2(A) can be improved by allowing the efg and hff to be different for the three sites (figure 2(B)). This results in a considerably higher efg combined with a somewhat lower magnetic hff at the parallel site (figure 3(b)). We cannot conclude whether this increase is an artefact from the fitting procedure in order to mimic a possible higher complexity of the magnetic order, or whether the parallel efg is really larger (e.g. due to a magnetostriction along [001]).

The two models proposed in figure 5 have consequences for other experimental techniques. At the centre of the cube, in both cases a small hff is created, which should be

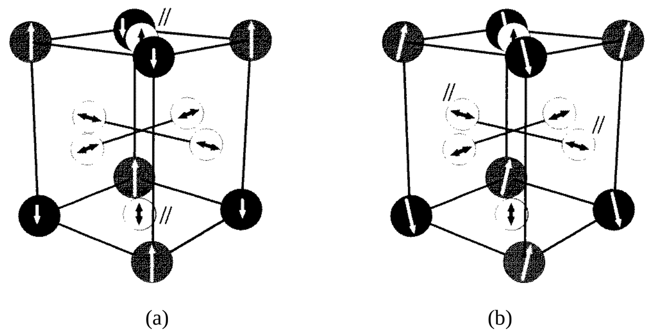


Figure 5. (a) The direction of the efg at the In position is indicated by a double arrow. If the U moments point along [001], and 'up' moments are larger than 'down', this yields a parallel efg and hff at the positions indicated with ∥ ($\beta_1 = 0°$) and a perpendicular efg and hff at the other positions ($\beta_2 = \beta_3 = 90°$). (b) If the U moments point mainly along [001] while 'up' and 'down' moments are tilted over an opposite small angle in the (010)-plane, again one-third of the positions have a parallel efg and hff ($\beta_2 = 0°$) and two-thirds are perpendicular ($\beta_1 = \beta_3 = 90°$).

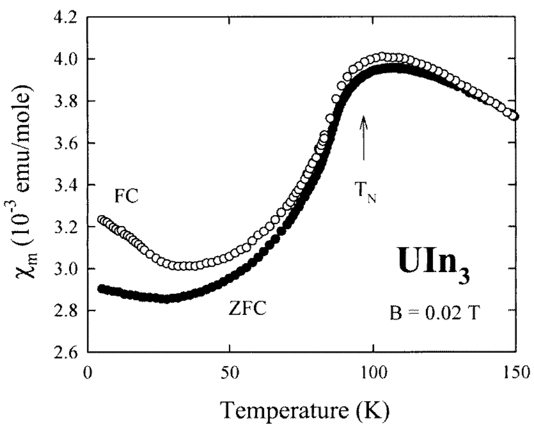


Figure 6. Low temperature magnetic susceptibility against temperature, measured on cooling the sample without (ZFC) and with (FC) an applied magnetic field of 0.05 T. The arrow marks the Néel temperature.

detectable by μSR. And indeed, although μSR measurements on UIn_3 [13] are interpreted as showing no sign of an hff, the authors note a change in the relaxation function which they attribute to irregularities in the magnetic structure. We claim that these measurements do notice the hff at the centre, which is obscured by the same effect that causes the deviations we see in the PAC measurements. A second consequence is the presence in both models of a small ferromagnetic component, which should be visible in magnetic susceptibility measurements. Indeed, as shown in figure 6, the temperature variation of the susceptibility of UIn_3 depends strongly on the magnetic history of the sample. A pronounced splitting of the $\chi(T)$ curves, taken upon cooling the sample in zero (ZFC) and non-zero (FC) magnetic field, indicates that UIn_3 is not a simple antiferromagnet with fully compensated magnetic moments but rather a canted or ferrimagnetic system. Thus the susceptibility data seem to corroborate our conclusions drawn from the PAC studies. This latter issue will be addressed in more extended manner in a forthcoming paper.

We finally draw attention to the fact that UIn_3 is part of the pseudo-binary system $U(In_{1-x}Sn_x)_3$, which is magnetic for $x < 0.5$. As will be discussed in detail elsewhere [14], the magnetic structure we found for UIn_3 also holds for the pseudo-binary.

4. Conclusions

The magnetic structure of UIn_3 is found to be of a slightly modified AFII type with U moments along [001]. Although the present results clarify the problem of different interpretations from Mössbauer measurements and yield the direction of the U moments, the fine details of the magnetic structure of UIn_3 still remain to be found. PAC on a small single crystal can give additional evidence of the [001]-orientation of the moments and can possibly give more information on the deviations found here. A refitting of the existing Mössbauer data set with our model would be a good test. Neutron diffraction on a single crystal might shed more light on how exactly the order deviates from AFII. However, for this sufficiently large single crystals are needed, which have not been grown successfully so far.

References

[1] Sanchez J P, Friedt J M, Shenoy G K, Percheron A and Achard J C 1976 *J. Phys. C: Solid State Phys.* C **9** 2207
[2] Murasik A, Leciejewicz J, Ligenza S and Misiuk A 1973 *Phys. Status Solidi* a **20** 395
[3] Krylov V I, Andreev A V, Sechovsky V and Havela L 1990 *Hyperfine Interact.* **59** 391
[4] Yuen T, Bykovetz N, Jiang G Y, Lin C L, Wise P P and Crow J E 1991 *Physica* B **171** 367
[5] Yuen T, Lin C L, Crow J E and Bykovetz N 1992 *J. Magn. Magn. Mater.* **109** 98
[6] Begum R J, Nagarajan R and Gupta L C 1993 *Physica* B **186–188** 714
[7] Schatz G and Weidinger A 1996 *Nuclear Condensed Matter Physics* (New York: Wiley) p 63
[8] Catchen G L 1995 *MRS Bull. (July)* 37–46
[9] Krishnamurthy V V, Mishra S N, Devare S H, Ramakrishnan S, Srinivas V and Chandra G 1993 *Hyperfine Interact.* **80** 1005
[10] Cottenier S, Toye A, Rots M, Spirlet J C and Winand J M 1995 *Physica* B **206/207** 492–4
[11] Forker M 1985 *Hyperfine Interact.* **24–26** 907
[12] Morin P and de Combarieu A 1975 *Solid State Commun.* **17** 975
[13] Kratzer A, Schopf C, Kalvius G M, Klauß H-H, Zwirner S and Spirlet J C 1997 *Hyperfine Interact.* **104** 181
[14] Cottenier S *et al* unpublished