High temperature tetragonal crystal structure of UPt₂Si₂

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Abstract

High temperature crystal structure of UPt₂Si₂ determined using single-crystal neutron diffraction at 400 K is reported. It is found that the crystal structure remains of the primitive tetragonal CaBe₂Ge₂ type with the space group P4/nmm. Anisotropic displacement factors of the Pt atoms at the 2a (3/4 1/4 0) and Si atoms at the 2c (1/4 1/4 z) Wyckoff sites are found to be anomalously large.

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I. INTRODUCTION

Uranium based intermetallic compounds have been a focus of an intensive research for many years due to their unique physical properties that arise mainly from a large extent of unfilled 5f-electron wave functions. [1] Their vicinity to the Fermi level and spatial extent leads to a sensitivity of these materials to external perturbations and existence of a vast number of crystallographic modifications. Many of the magnetic and bonding phenomena are due to a hybridization between 5f states and other electronic states in the solid and which controls for instance whether the system has localized or itinerant 5f magnetic states. As the hybridization depends on the number, distance of neighboring atoms (called ligands) and the geometry surrounding the 5f element it is extremely important to determine the details of the crystal structure. [1, 2] Tetragonal UT₂X₂ compounds (T stands for a late a transition metal and M for Si or Ge) comprising more than 20 members has been in the focus of scientific community for more than the last three decades. The most prominent member of the group, URu₂Si₂ exhibits an unconventional superconductivity |3-5| coexisting together with another, yet unknown, type of order [5]. Most of these compounds adopt the Th Cr_2Si_2 type of structure (space group I4mmm). [1, 2] However, few of them, namely those with T = Ir or Pt are reported to crystallize in the klassengleiche centrosymmetric subgroup $CaBe_2Ge_2$ type of structure with space group P4/nmm. [1, 6] Common for both these structures is the absence of $(h\ 0\ 0)$: h=2n+1 and $(h\ k\ 0)$: h+k=2n+1reflections that are systematically extinct due to an n-type glide plane.

The subject of this work is the confirmation of the UPt₂Si₂ crystal structure that is reported to adopt the latter, primitive version over the entire temperature range. [6–8] UPt₂Si₂ has been previously subject of numerous studies concentrated on the magnetic, transport and thermal properties. Particular attention has been devoted to the crystal and magnetic structures. [6–12] UPt₂Si₂ orders antiferromagnetically (AF) below T_N that is reported to range between 32 K and 35 K. [7, 10] It has been reported that the low-temperature AF structure is collinear with U moments of 1.9 - 2.5 μ_B , depending on a study,[7, 10] pointing along the c-axis direction. It can be described as a (up-down) stacking of ferromagnetic uranium sheets alternating along the tetragonal axis direction. Upon application of high magnetic fields it exhibits field-induced transitions for both, the a and c-axis directions with critical fields of about 40 T and 24 T, respectively.[1, 6–10] The field transition has been in-

terpreted as a topological Lifshitz transition.[11] Much attention has been paid to a possible crystallographic disorder [10] that has been linked to irreversibility in magnetic behavior.[12] Neutron powder and single crystal diffraction experiments have indicated that the one of the two Pt and Si atomic positions exhibit anomalously large displacement parameters.[10]

 UPt_2Si_2 exhibits near the room temperature, around $T_s \approx 315$ K, a significant specific heat anomaly. A discontinuity at similar temperature is seen also in the temperature dependence of the electrical resistivity. [8] As powder diffraction experiments did not revealed any significant changes in diffraction patterns, the origin of these anomalies remained for a long time a mystery. We then speculated that it is due to a crystal structure modification appearing at T_s . However, recently we have detected above T_s using a large UPt₂Si₂ single crystal glued to a sample holder very weak Bragg reflections violating the $(h\ 0\ 0)$: h=2n+ 1 (see Fig. 1 (a)) and $(h \ k \ 0)$: h + k = 2n + 1 extinction rules. The typical intensity ratio between these forbidden and allowed reflections was 1: 1000, i.e. much larger than possible contamination due to $\lambda/2$ contamination of the E4 neutron instrument. We continued speculating that the space group given in the literature is in error and that the glide plane connecting two of the Pt (and two Si) atoms is missing lowering the space group to P -4 2 m thereby splitting these sites into two independent sites. Different models were proposed, among them a different degree of occupation, mixing of atoms, different thermal factors at the two split sites and/or a subtle orthorhombic distortion have been considered. All these mechanisms would lead to an existence of forbidden reflections. The proximity of the structural transition leads to yet another possible scenario that the observed forbidden reflections are due to strain in the sample caused by the stiff glue. To be able to distinguish between different models we have undertaken a diffraction experiment on a relatively fresh small single crystal that was not cycled through the structural transition many times. Nevertheless, in order to determine the crystal structure at elevated temperatures, above the structural transition required a collection of a reasonable number of Bragg reflections, such a task is possible using the 4-circle instrument D9 at Institute Laue-Langevin (ILL), Grenoble. Neutron diffraction (instead of X-ray) has been used due to the presence of a heavy uranium that would make the x-ray determination difficult. Herein we report single crystal results of such a neutron diffraction study, which unambiguously confirms that UPt₂Si₂ forms in the centrosymmetric CaBe₂Ge₂ type structure.

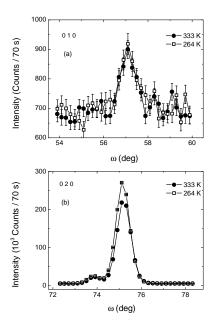


FIG. 1: Rocking curves through (a) the 010 and (b) the 020 reciprocal position of the UPt₂Si₂ single crystal recorded above $T_s \approx 315$ K, at 333 K (closed points) and below T_s at 264 K (open points), respectively.

II. EXPERIMENTAL

Single crystal of UPt₂Si₂ has been prepared by a modified tri-arc Czochralski method at the Leiden University. Characterization, including specific heat and high-field measurements can be found in literature. [8, 10, 13] For the diffraction experiments we have used two pieces originating from the same original large crystal. While at the Helmholtz-Zentrum Berlin (HZB) we have used ≈ 1.5 g heavy crystal of an irregular shape; at ILL a small bar-shaped, about 21 mg heavy crystal with dimensions $1 \times 1 \times 2$ mm³ with the longer dimension along the c-axis direction cut using spark-erosion has been used. Two separate diffraction experiments were carried out. At HZB we have used double-axis diffractometer E4 that that is equipped with a 200 x 200 mm³ position sensitive detector (PSD). The incident neutron wavelength of 2.41 Å produced by the Pyrolythic graphite PG(002) monochromator has been used. [14] Here we have collected data (typically 30 s per point) at temperatures from ≈ 260 K, i.e., below the specific heat anomaly up to ≈ 330 K, well above the T_s. At the ILL, the D9 hot neutron diffractometer with the incident wavelength $\lambda = 0.8377$ Å, operated in the four-

circle mode has been utilized. While in the former experiment the crystal has been glued to an aluminium holder, for the ILL experiment the crystal has been wrapped in an aluminium foil that has been fixed on the sample holder pin using dedicated high-temperature glue. In this way we have minimalized in the latter case the stress acting on the sample. Data were at D9 collected well above the structural transition temperature, at 400 K, achieved using a four-circle furnace. In order to be able to determine the crystal structure of UPt₂Si₂, we have recorded at D9 in total, 457 Bragg reflections, 292 of them unique. Among those were also 22 Bragg reflections that are forbidden for the space group P4/nmm. Allowed reflections were recorded with time 5 sec per point, forbidden ones mostly with 128 sec per point, in part with 300 sec per point. At both instruments, in order to reduce the $\lambda/2$ contamination, we have used additional filters. In both experiment, the orientational UB matrix has been calculated from several well centered Bragg reflections.

The crystal structure refinement has been performed using computer codes Fullprof [15]. Standard nuclear scattering lengths b(Pt) = 9.60 fm, b(Si) = 4.149 fm and b(U) = 8.417 fm were used. [16] For the absorption correction (Gaussian integration) we used the absorption coefficient $\mu = 0.15$ cm⁻¹. Anisotropic empirical extinction correction as implemented in Fullprof has been applied. Crystal structure has been drawn using graphical computer code VESTA. [17]

III. NEUTRON DIFFRACTION RESULTS

In Fig. 1 (a) we show rocking curves through the 010 reciprocal position of the UPt₂Si₂ single crystal recorded above T_s at 333 K (closed points) and at 264 K (open points), respectively. As can be seen, at both temperatures we observe the 010 Bragg reflection. This observation is rather striking as it suggests that the published crystal structure of UPt₂Si₂ is not correct. Namely, the $(h\ 0\ 0)$: h = 2n + 1 type reflections are forbidden for the P4/nmm space group.

While the intensity of the 010 Bragg reflection hardly changes across the T_s , Fig. 1 (b) documents that the 020 reflection increases. Indeed, as shown in Fig. 2 (a) and (c), the temperature dependences of the integrated intensities of these two reflections suggest that the 010 is temperature invariant whereas the 020 increases upon cooling. The different behavior of the two reflections is also seen in their diffraction angle value as shown in

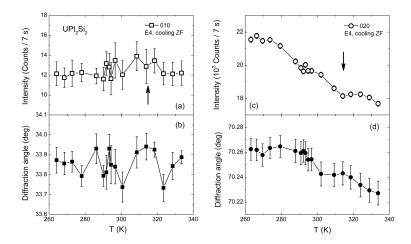


FIG. 2: Temperature dependence of the integrated intensities of (a) the 010 and (c) the 020 Bragg reflections measured on the large UPt₂Si₂ single crystal at E4 upon cooling across the anticipated crystal structure transition along with the respective diffraction angle at which the reflections appear ((b) and (d), respectively). Arrows denote the position of the anomaly seen on the temperature dependence of the specific heat that takes place around 315 K.

Fig. 2 (b) and (d). While the former reflection hardly changes its position, the 020 Bragg reflection shifts upon cooling to higher diffraction angles suggesting shrinking of the a-axis lattice parameter. Different behavior of the two Bragg reflections suggest that the 010 is not due to a finite $\lambda/2$ contamination although a non-zero contamination cannot be excluded even despite use of an additional filters. In addition, the increase of the 020 integrated intensity upon cooling from 333 K to 264 K is too large to be explained by the reduction of the displacement parameters. We propose that it is due to a crystal structure modification upon cooling across T_s . However, details of this transition will be published elsewhere. [19]

In order to verify the existence/non-existence of the $(h\ 0\ 0)$: h = 2n + 1 type reflections at elevated temperatures, we have performed the experiment using the D9 instrument. During this experiment we have paid attention to the $(h\ 0\ 0)$: h = 2n + 1 type reflections. In few cases a small intensity has been detected at these, for the P4/nmm space group forbidden reflection positions. These, however, have been proven to be due to small residual $\lambda/2$ contamination. These reflections vanished when an additional erbium $\lambda/2$ filter has been used.

In Fig. 3 (a) we show the experimental rocking curve through the 010 reciprocal point as recorded at D9 instrument at 400 K with measurement time of 300 sec per point utilizing an

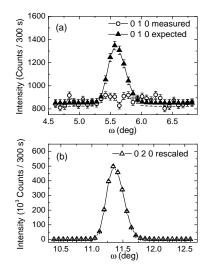


FIG. 3: (a) Rocking curve through the 0 1 0 reciprocal position of the UPt₂Si₂ single crystal recorded at 400 K using D9 instrument at ILL with measurement time of 300 s per point (open symbols) together with re-scaled intensity of the 0 2 0 Bragg reflection divided by a factor of 1000 (closed symbols), i.e. by the intensity factor between these reflections as observed in E4 experiment. (b) Experimental rocking curve through the 0 2 0 reciprocal position rescaled for the same time as in the (a) panel.

additional Er filter together with the expected intensity calculated from the rocking curve through the 020 Bragg reflection (see Fig. 3 (b)). The latter, expected, signal has been calculated with an assumption that the ratio between the 010 and 020 reflections would be similar as in the case of the E4 experiment. Clearly, we do not observe any intensity at the 010 reciprocal space position. This result is in disagreement with the experimental evidence from the E4 experiment.

IV. STRUCTURE REFINEMENT

In the course of the refinement, we have tested several crystal structure models. In particular, we have tried to to test solutions that allow for the (h00): h = 2n + 1 and (hk0): h + k = 2n + 1 type of reflections. Although not observed in the D9 experiment, E4 experiment has revealed the existence of these reflections. One has to survey all the non-isomorphic subgroups that do not contain the glide plane leading to extinction of above

mentioned forbidden reflections. There are only two such maximal subgroups, namely the P4mm and P4m2. We have looked for solutions that are close to the original CaBe₂Ge₂ type of structure. While we could not find any reasonable model with the former space group, with the latter it is possible to construct exactly this crystal structure. Within this space group splits original Pt1 and Si1 atomic positions into two inequivalent sites. However, although the extinction rules for the $P\overline{4}m2$ space group allow for all the (h00) and (hk0) reflections, these reflections would be still extinct if the atoms would occupy these sites with the same occupation and the same thermal displacement factors. In order to develop non-zero intensities on these reflections, these sites would need to be different. There are few possibilities to achieve this. First, the occupation could be different in terms of the percentage of atoms taking the respective sites. Second, there might be a finite preferential occupation or mixing of atoms among different sites. Third, the thermal displacement factors, isotropic or anisotropic, at different sites could be different. Combinations of the effects are, of course, possible as well. Nevertheless, it appears that the quality of fits allowing for these different possibilities is not better than conserving the original CaBe₂Ge₂ type of structure. Also attempts assuming a small orthorhombic distortion appear not to be significantly better.

The collected data set [18] described in Tab. I thus appear to be in agreement with the primitive tetragonal lattice. In accordance with the observed systematic extinctions, the centrosymmetric space group P4/nmm was found to be correct during the structure refinement. The starting positional parameters were obtained the literature. [6–8] Subsequently, the structural parameters were refined on the squared structure factors F^2 using anisotropic displacement parameters (ADPs) from all atoms. Plot of the observed versus calculated nuclear structure factors of UPt_2Si_2 after the extinction correction is shown in Fig. 4. The schematic representation of the UPt_2Si_2 crystal structure is shown in Fig. 5. The structure refinement reveals that the structure of UPt_2Si_2 is of the $CaBe_2Ge_2$ type.

The best fit to the data (see Fig. 4) leads the crystallographic parameters of the UPt₂Si₂ crystal structure, in particular the positional and the temperature displacement parameters, listed in Tab. II. The crystal structure is schematically shown in Fig. 5. The agreement between the observed and calculated structure factors is excellent, leading $R_F = 2.78$ if only isotropic displacement parameters factors and $R_F = 1.86$ if ADP are considered, respectively. Negligible occupational defficiency of the order of 1 % has been fount at the Pt1 2a (3/4).

TABLE I: Crystallographic data of UPt₂Si₂ single crystal and structure refinement information.

Empirical formula	UPt_2Si_2
$Molar weight (g mol^{-1})$	684.36
Crystal system	Tetragonal
Space group, Z	P4/nmm, 2
Temperature (K)	400
Unit cell dimensions (Å)	a = 4.2056(7)
	c = 9.709(4)
Calculated density (g cm^{-3})	13.23
Crystal size (mm ³)	$1\times1\times2$
Absorption coefficient (cm^{-1})	0.15
Θ range (deg)	9-85
Range in hkl	0+6, 0+4, -2+10
Number of reflections measured	457
Independent reflections measured	292
Observed reflections	216
Number of reflections with I $\stackrel{.}{\iota}$ 2σ	185
Number of free parameters	20
Number of restrains	0
Goodness of fit F^2	1.33
RF^2w -factor	2.20
χ^2	0.89

$1/4\ 0$) site.

The positional parameters refined given in Tab. II are very close to the literature values. [8] Inspection of the refinement parameters indicates an anomalous enhancement of the ADP for Pt1 atoms at the 2a and Si2 atoms at the 2c positions. These are, however, somewhat smaller than in the literature. [8] In Fig. 5 we also show the shortest Pt-Pt, Si-Si and Pt-Si bonds. The two crystallographically independent Pt atoms are coordinated differently by Si atoms that occupy also two independent sites. The Pt1 atoms are coordinated tetrahedrally by Si2 atoms, whereas the five neighbors of Pt2 are arranged in a square pyramid intersecting

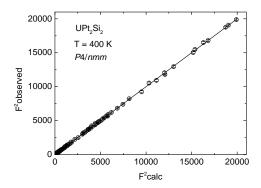


FIG. 4: Calculated versus observed structure factors squared recorded on UPt₂Si₂ single crystal at 400 K using D9 instrument at ILL.

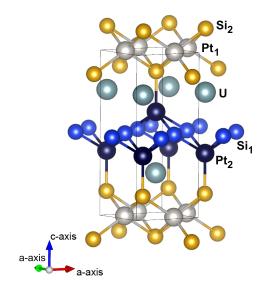


FIG. 5: A schematic representation of the tetragonal crystal structure of UPt₂Si₂ (CaBe₂Ge₂ type, space group P4/nmm) as determined from neutron diffraction data taken at D9 at 400 K. U atoms are shown as large (light blue), Pt atoms as intermediate (gray and dark blue), and Si atoms as small (blue and orange) spheres, respectively. Bonds highlight the nearest neighbor Pt-Pt, Si-Si and Pt-Si distances.

the plane made of U atoms. Interatomic distances are listed in Tab. III. As can be seen, the PtSi distances range from 238 to 247 pm, i.e. somewhat smaller than the sum of the covalent radii for Pt + Si of 247 pm. [20] This illustrates to a very strong bonding between Pt and Si. The largest neighbor Pt-Si distance is found between for Pt1 atoms at the 2a and

TABLE II: Crystal structure parameters of a UPt₂Si₂ single crystal determined from neutron diffraction data set obtained above T_s, at 400 K at D9 (ILL). For symmetry reasons are $U_{11} = U_{22}$ and the values U_{12} , U_{13} , and U_{23} of all the atoms in the structure are equal to zero. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} . Standard deviations are given in parentheses.

T=4	T = 400 K S.G.: $P4/nmm$							
Atom	Site	x/a	y/a	z/c	occ.	U_{11}	U_{33}	U_{eq}
						$(\mathring{\rm A}^{-2})$	$(\mathring{\rm A}^{-2})$	$(\mathring{\rm A}^{-2})$
U	2c	1/4	1/4	0.74833(4)	1.00(f)	0.0073(2)	0.0014(1)	0.0066(2)
Pt1	2a	3/4	1/4	0	0.989(3)	0.0175(2)	0.0021(1)	0.0139(2)
Pt2	1c	1/4	1/4	0.37868(4)	1.001(1)	0.0067(2)	0.0015(1)	0.0063(2)
Si1	2b	3/4	1/4	1/2	1.000(1)	0.0076(3)	0.0019(1)	0.0076(2)
Si2	2c	1/4	1/4	0.13357(4)	0.996(2)	0.0123(4)	0.0014(2)	0.0095(3)
Agreement factor: $R_F = 1.86$								

Si2 atoms at the 2c positions, for which also an enhanced ADP values are found (see Tab. II). Let us note that the same atoms (Pt1 and Si2) are constitute a buckled layer (see Fig. 5) suggesting that these pairs of atoms might be susceptible to severe distance modifications thus making the crystal structure potentially unstable. Nevertheless, our present data do not indicate any form of modification/distortion from the CaBe₂Ge₂ type structure.

V. CONCLUSIONS

It is now clear that UPt_2Si_2 adopts at high temperature above the structural transition around T_s the $CaBe_2Ge_2$ type structure with the space group is P4/nmm. This result is in agreement with the literature [1, 2]. The existence of the forbidden reflections of the $(h\ 0\ 0)$: h=2n+1 and $(h\ k\ 0)$: h+k=2n+1 type seen in E4 experiment using a large single crystal glued rigidly on a sample holder are explained to be due to internal strain in the crystal. We speculate that the crystal structure of this system should be very sensitive to the application of pressure, especially around room temperature. In conclusion, the D9 neutron diffraction experiment using small single crystal free of strain shows that the high temperature crystal structure of UPt_2Si_2 is of the expected $CaBe_2Ge_2$ type.

TABLE III: Interatomic distances in UPt₂Si₂ as determined from the D9 neutron diffraction experiment at 400 K.

Atom Neighbor Number Distance Atom Neighbor Number Distance

			$(\mathring{\mathrm{A}})$				(Å)
U:	Si2	4	3.187	Pt2:	Si2	1	2.380
	Si1	4	3.199		Si1	4	2.410
	Pt2	4	3.219		U	1	3.219
	Pt1	4	3.224		U	4	3.589
	Pt2	1	3.589	Si1:	Pt2	4	2.410
	Si2	1	3.740		Si1	4	2.974
	U	4	4.206		U	4	3.199
Pt1:	Si2	4	2.471	Si2:	Pt2	1	2.380
	Pt1	4	2.974		Pt1	4	2.471
	U	4	3.224		U	4	3.187
					U	1	3.740

Acknowledgments

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