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Crystal structure assignment for the heavy-fermion superconductor UPt_3

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Understanding the normal and superconducting states in UPt_3 depends critically on its crystal structure. Based on high-energy x-ray diffraction and transmission electron microscopy, we have determined that the crystal structure of UPt_3 is trigonal, not hexagonal as traditionally held. Its trigonal structure provides an interpretation of recent high-field muon spin rotation experiments and may be relevant to the existence of the symmetry-breaking field required by most theoretical models of heavy-fermion superconductivity.

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Unconventional superconductors, whose order parameters have a lower symmetry than the normal state, pose a challenge to condensed-matter physics because their complex, anisotropic behavior does not obey BCS theory. The heavy-fermion superconductor UPt_3 has received considerable attention because it clearly exhibits unconventional behavior, having multiple superconducting phases with coexistent antiferromagnetic order, although the precise nature of the antiferromagnetism is still not completely understood.[1,2] The physics of many heavy-fermion materials is complicated by questions regarding the role of surfaces, incommensurate or superstructure modulations, and minority phases. Nevertheless, UPt_3 has become a preferred material for studying unconventional superconductivity in the heavy fermions because very large, high-purity crystals can be grown.[3] After discovery by Stewart *et al.*,[4] indications of the unconventional nature of its superconducting state led to extensive interest in this compound.[1,2] Compelling evidence that UPt_3 was in this class followed from the observation of multiple superconducting phases in the magnetic field versus temperature phase diagram.[5,6] Developments based on theoretical analysis of the low-temperature transport properties narrowed the number of viable theoretical models to the two-dimensional orbital pairing states with even or odd parity. The theory based on odd-parity pairing[7] has been very successful in explaining the phase diagram and the transport properties of UPt_3. Yet most such analyses have been based on the view that the symmetry of UPt_3 is hexagonal, with some weak symmetry-breaking field.[1,2] Our transmission electron microscopy (TEM) and high-energy x-ray-diffraction studies show that the actual crystal structure has trigonal symmetry. Only with complete knowledge of the bulk crystal structure can we fully understand a material's normal state and low-temperature properties. In particular, the present crystal structure determination leads to a natural interpretation of muon spin resonance in UPt_3;[8] a simple explanation of these measurements is not possible with the assumption of hexagonal symmetry.

UPt_3 was found originally by Heal and Williams to have the $D0_{19}$ alloy structure.[9] Such hexagonal close-packed materials have the space group $P6_3/mmc$, with U atoms at the $2c$ site in Wyckoff notation (having $\overline{6}m2$ site symmetry, i.e., invariant under sixfold rotation plus inversion) and Pt atoms at the $6h$ site[10] as shown in Fig. 1. Atoms at both sites are constrained to be at height $z=\pm\frac{1}{4}$. The only free structural parameter is x_{Pt}, which determines the in-plane coordinates of the Pt atoms (see Fig. 1). Lacking the necessary sensitivity in their x-ray powder-diffraction studies to refine this parameter, Heal and Williams assumed the ''ideal'' value $x_{\mathrm{Pt}}=\frac{5}{6}$, which has been accepted since. A recent neutron-scattering study by Keizer *et al.*, however, determined x_{Pt} is either 0.8253 or 0.8370, based on a comparison of intensities from two nuclear Bragg peaks.[11] Calculations by Farkas suggest that values of $x>\frac{5}{6}$ may be expected for atoms in the $6h$ site of $D0_{19}$ alloys.[12] Yet our diffraction studies of UPt_3 indicate that this relaxation from ''ideal'' hexagonal behavior does not fully describe the crystal structure of UPt_3 and that a lower symmetry space group is required.

We have performed detailed TEM studies of the nanostructure of UPt_3 subjected to different annealing

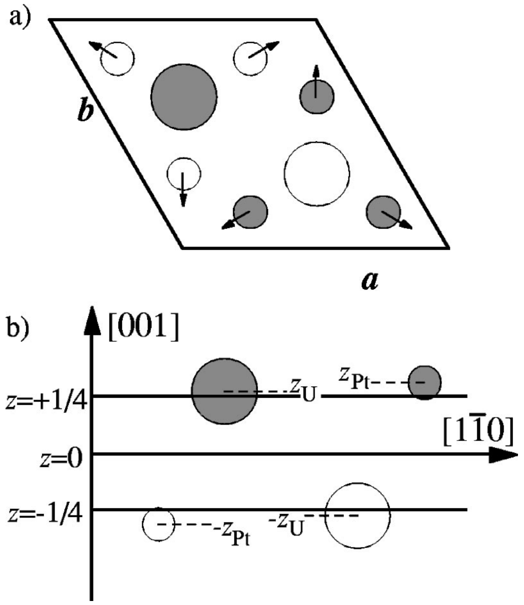

FIG. 1. Unit cell of UPt_3. Large circles are U atoms, located at $\pm(\frac{1}{3},\frac{2}{3},z_U)$ in fractions of the unit cell. Small circles are Pt atoms at $\pm(x_{Pt},2x_{Pt},z_{Pt})$, $\pm(x_{Pt},\overline{x_{Pt}},z_{Pt})$, and $\pm(\overline{2x_{Pt}},\overline{x_{Pt}},z_{Pt})$. (a) Projection down the c axis: The circles for Pt atoms are drawn at the ''ideal'' value $x_{Pt}=\frac{5}{6}$, with arrows pointing toward increasing x_{Pt}. Dark and open circles are at the heights $+z$ and $-z$, respectively. (b) Cross-section along the long diagonal: For trigonal symmetry $z_U \neq z_{Pt}$, but for hexagonal space groups $z_U = z_{Pt} = \frac{1}{4}$.

treatments.[13] Surprisingly, the observed transmission electron-diffraction patterns are inconsistent with $P6_3/mmc$ symmetry as we clearly observe reflections that violate the extinction condition $(P--c)$ of this space group. Specifically, reflections of the type $(h,\overline{2h},l)$ should be systematically absent for odd values of l. This is *not* the case, as seen in the electron diffraction pattern displayed in Fig. 2. ''Forbidden'' reflections were found in many diffraction patterns taken along various crystallographic orientations,[13] so this is not a multiple-scattering effect. Instead, the presence of these reflections indicates that UPt_3 has a space group with lower symmetry than $P6_3/mmc$. Multiple scattering can, however, complicate the quantitative interpretation of transmission electron-diffraction intensities. We have therefore performed high-energy x-ray-diffraction measurements to determine precisely the space group of UPt_3 and, in particular, the site symmetry of the U atoms. In this paper, we present the first detailed structural determination of UPt_3 made with a full array of modern crystallography techniques.

The UPt_3 crystals were grown in an ultrahigh vacuum, float-zone refining system[3] using indirect electron-beam heating. Subsequent long-term annealing treatments were performed on different samples, also in ultrahigh vacuum, at temperatures between 800 and 1300° C, resulting in crystals with high crystal quality and very low impurity concentrations.[3] Samples for TEM were prepared by mechanical thinning followed by low-energy ion milling to a thickness of less than 50 nm, necessitated by the high mass of UPt_3. X-ray samples of $\sim$200-μm size were etched in acid to remove damaged surface layers. X-ray-diffraction measurements were performed at the DuPont-Northwestern-Dow Collaborative Access Team beamline 5BM-D of the Advanced Photon Source, Argonne National Laboratory. Data were collected using the oscillation method on a MAR two-dimensional charge-coupled device camera. 75-keV x rays ($\lambda = 0.165$ Å) were selected from bending magnet radiation by a Si(111) double-crystal monochromator, with the second crystal held at 75% detuning. High-energy x rays were essential for minimizing absorption (linear absorption coefficient $\mu \approx 47\ \mathrm{cm}^{-1}$ at 75 keV but is greater than 1000 cm^{-1} at 20 keV). Given the large electron density of UPt_3, a high-resolution experiment with bulk sensitivity was feasible only at a high-energy synchrotron source that could provide a sufficient intensity of high-energy x rays. In most cases, samples were cooled to 130 K using a nitrogen gas cold

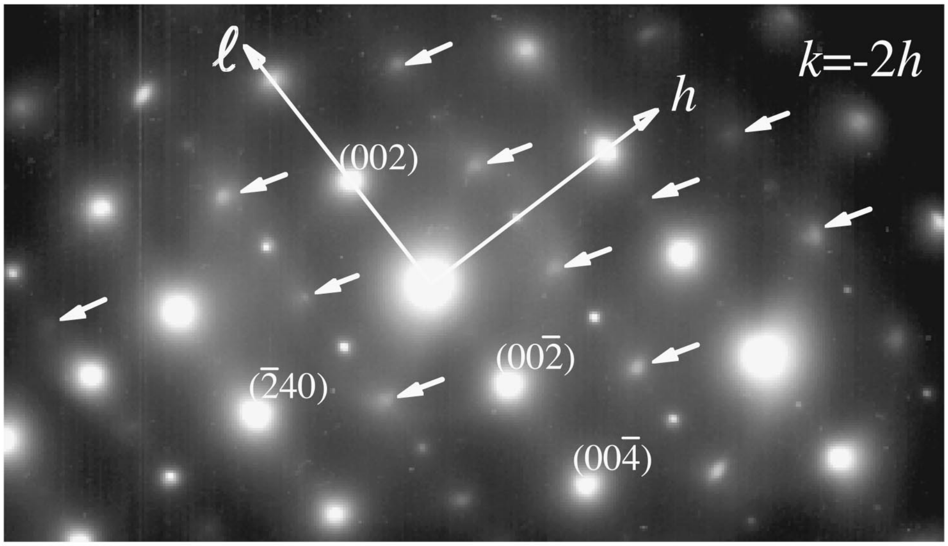

FIG. 2. A transmission electron diffraction pattern of UPt_3 in the $(h,\overline{2h},l)$ plane. Several reflections forbidden by the extinction condition of the traditionally assumed hexagonal space group $P6_3/mmc$ are marked by arrows.

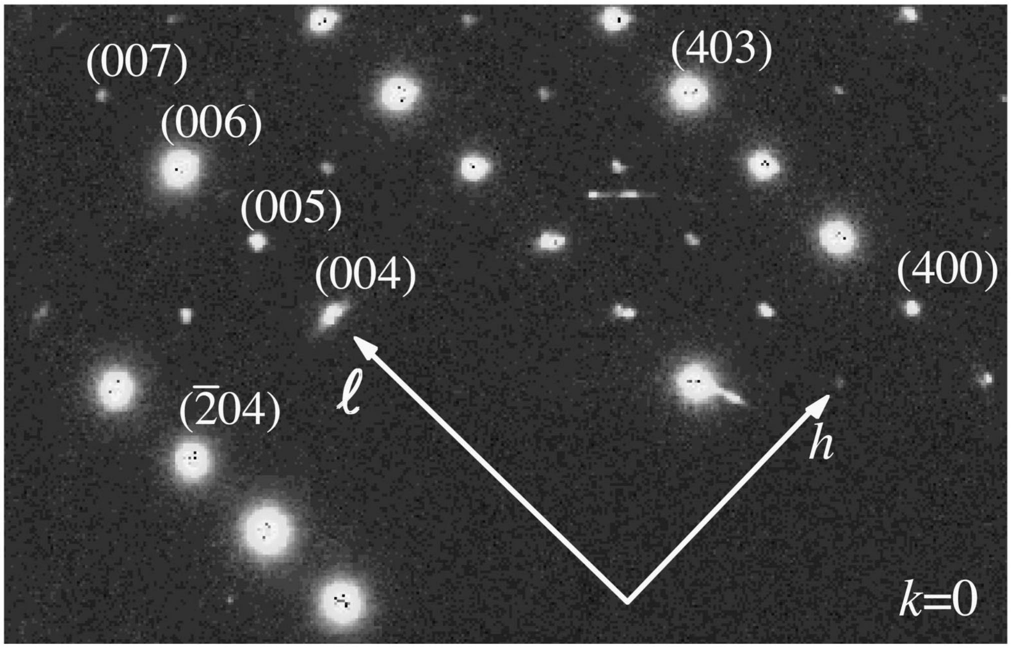

FIG. 3. A portion of an x-ray oscillation diffraction pattern of UPt_3, in the $(h0l)$ plane. The oscillation range is 3°. The (005) and (007) reflections are inconsistent with a hexagonal close-packed structure, or with any structure made of equally spaced atomic planes along [001].

stream, but no structural changes were observed between 130 K and room temperature. Integrated intensities were extracted with the HKL suite of programs,[14] and structure refinement was performed with the program SHELXL.[15]

A portion of an x-ray-diffraction pattern from a UPt_3 sample, annealed at 970° C for six days, is shown in Fig. 3. This sample had a very high residual resistivity ratio of 741 and a very narrow superconducting transition ($\Delta T_c = 6.8$ mK, $T_c = 0.546$ K); all samples investigated had clear double transitions.[3] We present detailed results for this crystal measured at 130 K, for which diffraction data was collected to a resolution of 0.3 Å. Similar to the TEM diffraction pattern shown in Fig. 2, reflections forbidden by $P6_3/mmc$ symmetry are present. The ratio of integrated intensity to statistical error for many of the measured ‘‘forbidden’’ reflections is greater than 20. Furthermore, we have shown, using an energy-sensitive detector,[16] that these reflections are not due to the second harmonic of the x-ray beam.

The combined evidence of the TEM and x-ray-diffraction patterns leads us to conclude that no reflections are systematically absent for UPt_3 (i.e., extinction symbol P−−−). This is inconsistent with the traditionally assigned space group $P6_3/mmc$. Still, the x-ray diffraction pattern appears to have hexagonal symmetry, with Laue class $6/mmm$. Namely, merging symmetry-equivalent reflections based on Laue class $6/mmm$ yields results just as good as merging with trigonal symmetry. Normally it would be reasonable to take the highest apparent symmetry as the correct one for a crystal. For UPt_3, however, none of the hexagonal space groups with P−−− extinction is compatible with the known density (two formula units per unit cell) and with reasonable interatomic distances (e.g., the U-U separation would be only 3.3 Å for space group $P6/mmm$). Instead, the atoms of the unit-cell experience very slight vertical displacements, lowering the crystal symmetry from hexagonal to trigonal. Thus, the requirement that all atoms be located at $z = \pm\frac{1}{4}$ is relaxed, and in general $z_U \neq z_{Pt}$. Specifically, we find that the data can be explained in the trigonal space group $P\bar{3}m1$, with U atoms in the $2d$ site and Pt atoms in the $6i$ site.[10] While the space group is still centrosymmetric, the site symmetry of the U atoms is reduced substantially from $\bar{6}m2$ to $3m$. Similarly, the site symmetry of the Pt atoms changes from $mm2$ to $.m$.

With the space group $P\bar{3}m1$, the Laue class of UPt_3 is $\bar{3}m$. The reason that the Laue class appears to be $6/mmm$ is that our samples are twinned by merohedry. Merohedry means the samples consist of two sets of twin domains oriented such that their reciprocal lattices exactly overlap.[17,18] For ‘‘perfect’’ merohedral twinning, the two twins possess equal volume fractions, which increases the apparent Laue symmetry.[19] Although the ‘‘forbidden’’ reflections preclude UPt_3 from being hexagonal, perfect merohedral twinning gives trigonal UPt_3 a hexagonal diffraction pattern. Solutions with atomic coordinates $z > \frac{1}{4}$ and $z < \frac{1}{4}$ lead to equivalent crystal structures; twinning arises because both solutions appear in separate parts of a given sample. In a separate experiment,[16] we collected high-energy diffraction data on a four-circle diffractometer. Line-shape analysis indicates the characteristic size of a twin is only ~200 Å. Thus these large samples have many individual twin domains (roughly on the order of 10^{12}), probably because the energy barrier to twinning is very small. Since neither twin orientation is preferred during growth, both occur with nearly equal frequency and perfect merohedral twinning results.

Table I lists the crystallographic variables from the best-fit solution, along with substantially worse fits assuming hexagonal symmetry. We show both ‘‘ideal’’ hexagonal, with

TABLE I. Refined crystallographic parameters and Bragg-Williams factor from high-energy x-ray diffraction of UPt_3 annealed at 970° C. Measurement temperature is 130 K; $a=5.712$ Å, $c=4.864$ Å. $R1$ is the linear, unweighted residual for all 1152 unique reflections, including those forbidden by the given symmetry. The $P\overline{3}m1$ refinement included perfect merohedral twinning.

Symmetry	$R1$	x_{Pt}	z_{Pt}	z_{U}	S_{BW}
''Ideal''	18.5%	5/6	1/4	1/4	1.00
$P6_3/mmc$	3.78%	0.83695(3)	1/4	1/4	0.99
$P\overline{3}m1$	2.45%	0.83692(2)	0.25210(6)	0.25069(10)	0.98

$x_{\mathrm{Pt}}=\frac{5}{6}$, and the best-fit hexagonal solution, in which x_{Pt} is a variable. The refined values of x_{Pt} are very close to one of the values proposed by Keizer *et al.*[11] Also shown are refined values of the Bragg-Williams parameter S_{BW};[20] these high values (near unity) are indicative of a well-ordered intermetallic compound. Attempts to fit the data within a trigonal space group of still lower symmetry ($P\overline{3}$ or $P321$) did not result in a better fit.[21] The anisotropic thermal parameters U_{ij} for the best fit are shown in Table II.

The observed deviation from hexagonal symmetry is not due to extrinsic or minority-phase effects. We did not detect any peaks corresponding to the off-stoichiometric phases UPt_2 or UPt_5. Stacking faults could lead to streaks in the diffraction pattern, but not to the sharp spots we observe. Our observations cannot be explained by a double hexagonal close-packed phase as reported by others,[22] since that leads to more *stringent* extinction conditions. Nor was there any evidence for an incommensurate modulation in either our TEM or x-ray experiments as suggested previously.[23]

The finding of trigonal symmetry for UPt_3 immediately raises the question of why this lower symmetry has not been previously identified. The answer to this question lies primarily in the very small extent to which hexagonal symmetry is broken. The deviations of z_{U} and z_{Pt} from their hexagonal values are very small, less than 0.01 Å. Such differences would not be *a priori* expected for such an apparently simple material, and may not be observable in a low-resolution experiment, especially if not explicitly searched for. A secondary reason that trigonal symmetry was not identified earlier via diffraction is the high electron density, which made detailed x-ray-diffraction studies unfeasible except at high-energy synchrotron sources. Conventional x-ray sources at lower energies suffer from very large absorption effects, making it difficult to measure accurately the relatively weak ''forbidden'' reflections.

TABLE II. Anisotropic thermal parameters of UPt_3 at 130 K, as given by structure refinement in $P\overline{3}m1$. Symmetry independent parameters are given in units of 10^{-3} Å^2, otherwise symmetry constraints are shown. Refinement in $P6_3/mmc$ leads to very similar values, although $U_{23}=U_{13}=0$ for the Pt atom by symmetry.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	1.91(4)	U_{11}	2.40(5)	0	0	$U_{11}/2$
Pt	2.26(4)	2.45(6)	2.69(5)	$-0.25(10)$	$U_{23}/2$	$U_{22}/2$

These results shed light on the normal-state properties of UPt_3. The vertical displacements explain why UPt_3 is the only (supposed) $D0_{19}$ alloy whose c/a ratio, 0.852, is significantly *greater* than 0.816, the ideal value predicted by close packing spherical atoms.[24] The z values differing from $\frac{1}{4}$ cause a vertical lattice expansion, increasing the c/a ratio. We do not expect to find more cases of trigonal symmetry in the rest of the $D0_{19}$ alloys, since the c/a ratios in all other such compounds are much closer to the ideal hexagonal value; compared to similar binary alloy systems, UPt_3 seems unique in its low symmetry.

Our finding that UPt_3 is trigonal provides a natural explanation to recent high-field muon spin rotation (μSR) studies, which cannot be fully interpreted assuming hexagonal symmetry. Specifically, Yaouanc *et al.* observed a splitting of the μSR signal when the external field B_{ext} was parallel to a. No splitting was observed for $B_{ext}\|c$. Yaouanc *et al.* concluded from their data that UPt_3 is somehow inhomogeneous, consisting of two regions with equal volumes, even though the muon occupies only one magnetic site.[8] Following the work by Schenck *et al.*[25] on $U(Pt_{0.95}Pd_{0.05})_3$, that site was assumed to be (000) and, implicitly, $(00\frac{1}{2})$, which is a symmetry-equivalent site in $P6_3/mmc$. However, for the trigonal space group $P\overline{3}m1$, these sites are *not* equivalent. We propose that muons occupy both (slightly inequivalent) sites, which splits the signal for $B_{ext}\|a$. Slight differences in the sites' magnetic fields may give rise to the complicated μSR signal near the Néel temperature.[8] As a local probe, μSR is sensitive to local crystal structure and will not average over nearly identical sites, as bulk susceptibility measurements and some other macroscopic probes do.

The trigonal crystal symmetry of UPt_3 leads us to take a fresh look at the low-temperature properties, including the order parameter of the superconducting state. Previously, the most likely candidates for the order parameter symmetry had been considered to be E_{1g} or E_{2u}, corresponding to even- and odd-parity respectively. For trigonal symmetry, however, the E_{1u} and E_{2u} representations in hexagonal symmetry become degenerate, to E_u. Similarly, E_{1g} and E_{2g} become E_g. Therefore the most general order parameter would be either E_g or E_u. Comparison of thermal conductivity,[26,27] sound attenuation,[28] and flux-line lattice[29] experiments with theory[7] indicates odd parity E_u is correct. Beyond this change in nomenclature, one might expect trigonal symmetry to add little intermixing, perhaps only on the order to which hexagonal symmetry is broken; if so, the theoretical interpretation of these experiments is unlikely to be affected. It is, however, possible that the trigonal crystal structure is relevant to the phenomenological models which require a static symmetry-breaking field to understand the multiple superconducting phases of UPt_3.

In summary, we have used high-energy x-ray diffraction and transmission electron microscopy to determine that the crystal structure of UPt_3 is trigonal. The local symmetry at the uranium atom site is threefold, rather than the previously accepted $\overline{6}$ symmetry. Our results have a direct impact on the interpretation of normal and superconducting properties of this important compound.

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