Refined crystal structure of UPt_3

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Introduction

We used high-energy x-ray diffraction to refine the crystal structure of UPt_3, a heavy Fermion material whose low-temperature properties (superconductivity and antiferromagnetism) have been widely studied but are not completely understood. While a number of experiments have established UPt_3 as an unconventional superconductor [1], a consensus has not yet emerged regarding the symmetry of the superconducting order parameter. Here we present evidence that the bulk crystal structure of UPt_3 at 130 K possesses lower symmetry than originally believed, which could have significant ramifications on the low-temperature properties of this material.

Methods and Materials

Nominally single-crystal samples of UPt_3 were grown by ultrahigh vacuum float-zone refining with subsequent annealing from 800°C to 1300°C, resulting in high crystal quality and very low impurity concentrations. X-ray diffraction measurements were performed at beamline 5-BM-D of DND-CAT, Advanced Photon Source. Data were collected using the oscillation method on a two-dimensional CCD camera with 75 keV x-rays (λ = 0.165 Å). High-energy x-rays were essential for minimizing absorption; given the large electron density of UPt_3, a high-resolution experiment was feasible only at a high-energy synchrotron source that could provide a sufficient intensity of high-energy x-rays. Integrated intensities were measured with the HKL suite of programs [2] and were fit with SHELX [3]. There were no peaks corresponding to the off-stoichiometric phases UPt_2 or UPt_5.

Results

The experimental diffraction patterns (typically consisting of >1500 independent reflections per sample, to a resolution of 0.3 Å) were of apparent Laue class 6/*mmm*, but were inconsistent with the $P6_3/mmc$ space group traditionally assigned to UPt_3 [4].

That is, the systematically absent reflections required by $P6_3/mmc$ symmetry were, in fact, present throughout the diffraction pattern. Furthermore, the data cannot be reconciled with any hexagonal space group. Instead, the atoms of the unit cell experience very slight vertical displacements, lowering the crystal's symmetry to a trigonal space group, as shown in Figure 1. Careful data collection was required to accurately measure the displacements of the atoms from their "ideal" hexagonal positions (displacements were less than 1% of the unit cell length). The "single" crystal is, however, twinned by merohedry, with equally populated twins that give the appearance of hexagonal symmetry. With this lowering the symmetry of the space group, the symmetry of the U site (the source of the superconducting and magnetic properties) is substantially reduced from $\bar{6}m2$ to $3m$. Table 1 compares the fitting results from the two space groups, demonstrating the significantly better fit for the lower symmetry $P\bar{3}m1$. Data were also fit with anisotropic Debye-Waller factors and an extinction factor [3], and a Bragg-Williams order parameter that refined to nearly unity, indicative of a well-ordered alloy. Further reductions to the symmetry of the space group (to either $P\bar{3}$ or $P321$) did not result in a better fit.

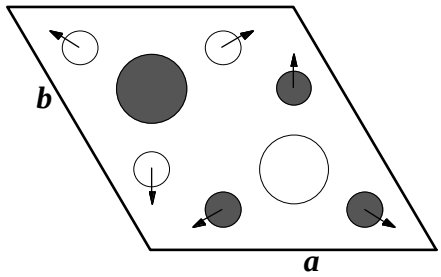

Figure 1: Unit cell of UPt_3 viewed down the *c* axis. Large circles are U, small circles are Pt. Dark and open circles are at heights $+z$ and $-z$, respectively. For trigonal symmetry $z_U \neq z_{Pt}$ in general, but for hexagonal space groups $z_U = z_{Pt} = 1/4$. Arrows indicate the possible in-plane displacement of Pt atoms permitted in $P6_3/mmc$ and $P\bar{3}m1$ space groups.

Table 1: High-energy diffraction results for UPt_3

Space group	$P6_3/mmc$ **(hexagonal)**	$P\bar{3}m1$ **(trigonal)**
R1 (unweighted residual)	3.8%*	2.4%
x_{Pt}	0.837	0.837
z_{Pt}	1/4†	0.2521
z_U	1/4†	0.2507

*For all measured reflections, including those forbidden by this space group.
†Fixed by symmetry.

Discussion

Our results significantly restrict the possible symmetry of the superconducting order parameter (which in the past was often assumed to have six-fold symmetry) and will help complete the theoretical description of the low-temperature properties of this surprisingly complex material.

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