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Structure of the Heavy-Fermion Superconductor UBe_{13}*

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Abstract. Uranium–beryllium, UBe_{13}, $M_r = 355\cdot2$, cubic, $Fm3c$, $a = 10\cdot268$ (2) Å, $V = 1082\cdot5$ Å^3, $Z = 8$, $D_x = 4\cdot359$ g cm^{-3}, λ(Mo $K\alpha_1$) = 0·70926 Å, $\mu = 282\cdot8$ cm^{-1}, $F(000) = 1066\cdot4$, room temperature, final $R = 0\cdot022$ for 74 observed independent reflections $[I > 2\sigma(I)]$ out of 937 measured reflections. This is the first single-crystal study of the heavy-fermion superconductor UBe_{13}. The U is surrounded by eight dodecahedral cages each containing one Be(1) at the center, encompassed by Be(2). The U—Be(2) distance is 3·013 Å while the Be(1)—Be(2) distance is 2·163 Å.

Introduction. The discovery of superconductivity in UBe_{13} and a few other heavy-fermion systems stimulated an intensive effort to characterize the nature of both the normal and superconducting states of these materials. In the normal state the electronic specific heat coefficient, γ, of UBe_{13} extrapolates to a $T =$ 0 K value of 1·1 J mol^{-1} K^{-2} (Ott, Rudigier, Fisk & Smith, 1983). The specific heat jump of about 1 J mol^{-1} K^{-1} at the superconducting transition temperature suggests that the f electrons responsible for the heavy masses are also responsible for the superconductivity. Although there have been previous structural studies on polycrystalline UBe_{13} (Baenziger & Rundle, 1949; Goldman, Shapiro, Cox, Smith & Fisk, 1985), this work represents the first such study on single-crystal UBe_{13}.

Experimental. Crystals of UBe_{13} were obtained by slow cooling from an aluminium flux. Crystal dimensions were 0·02 × 0·03 × 0·04 mm. CAD-4 diffractometer, θ–2θ scans. θ scan range (0·8 + 0·34 tanθ)°. Scan speed 1·0 to 8·2° min^{-1}. Background first and last one-sixth of scan range. Graphite-monochromated Mo $K\alpha$ radiation. Unit cell from 25 reflections, $7 \leq \theta \leq 23°$. Empirical ψ scan and spherical absorption corrections, transmission = 0·39–0·25. $(\sin\theta/\lambda)_{max} = 0\cdot7023$ Å^{-1}. Index range $0 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 14$. Standard reflections $22\bar{4}$, $22\bar{6}$, max. r.m.s. variation 1·5% with no trends. $R_{int} =$ 0·027 from merging equivalent reflections in original data set containing 937 measured reflections, resulting in 74 observed reflections $[I > 2\sigma(I)]$ out of 83 measured independent reflections. Least-squares refinement minimized $\sum w(\Delta F)^2$, $w = [\sigma_c^2(F) + 0\cdot030F^2]^{-1}$, $\sigma_c^2(F)$ based on counting statistics. Scale factor, isotropic type-II extinction parameter (Zachariasen, 1967; Larson, 1967), positional parameters, anisotropic thermal parameters for Be(2), $R = 0\cdot022$, $wR = 0\cdot028$, $S = 1\cdot715$, final $(\Delta/\sigma)_{max} = 0\cdot037$. Final ΔF Fourier synthesis $-1\cdot96 \leq \rho \leq 1\cdot63$ e Å^{-3}. The single large peak is 0·6 Å from the U atom. Scattering factors f, f' and f'' from *International Tables for X-ray Crystallography* (1974). Calculations on a Cray 1 using the Los Alamos Crystal Structure System developed primarily by A. C. Larson (Larson, 1977).

Discussion. Final parameters are listed in Table 1.‡ The numbering scheme is shown in Fig. 1. Bond lengths are given in Table 2. The cell constants are consistent with previous X-ray powder-diffraction measurements on samples of a single crystalline

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‡ A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52688 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

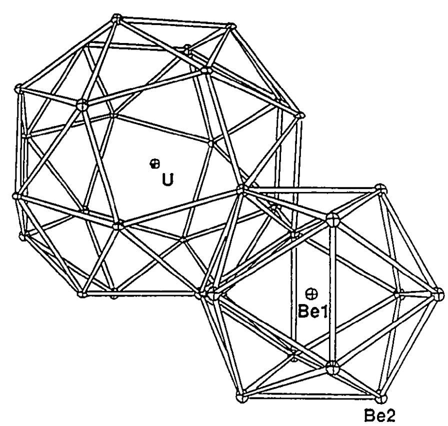

Fig. 1. The nearest neighbors of U (irregular snub cube) and Be(1) (irregular icosahedron).

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Table 1. *Fractional coordinates and thermal parameters* (Å^2)

	x	y	z	B		x	y	z	B
U	0·0250 (0)	0·250 (0)	0·250 (0)	0·38 (5)	Be(1)	0·000 (0)	0·000 (0)	0·000 (0)	0·6 (5)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Be(2)	0·000 (0)	0·1151(9)	0·1765 (9)	0·8 (3)	1·2 (3)	0·9 (4)	0·0 (0)	0·0 (0)	−0·3 (3)

The anistropic temperature factor is $\exp[-2\pi^2(U'_{11}h^2 + U'_{22}k^2 + U'_{33}l^2 + U'_{12}hk + U'_{13}hl + U'_{23}kl)]$, where $U'_{ij} = U_{ij}a^*_i a^*_j$ and U_{ij} is multiplied by 100.

Table 2. *Nearest-neighbor distances in* UBe_{13}

Bond to atom	Number of bonds	d (Å)
Bonds involving U		
Be(2) $(0,y,z)$	24	3·013 (5)
Bonds involving Be(1)		
Be(2) $(0,y,z)$	12	2·163 (9)
Bonds involving Be(2)		
U $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	2	3·013 (5)
Be(1) (0,0,0)	1	2·163 (9)
Be(2) $(0,z,\frac{1}{2}-y)$	2	2·231 (9)
Be(2) $(z,0,y)$	4	2·25 (1)
Be(2) $(0,-y,z)$	1	2·3635 (7)
Be(2) $(y,0,\frac{1}{2}-z)$	2	2·25 (1)

phase, which are different from the cell constants obtained for polycrystalline-phase material (Smith *et al.*, 1985). The material consisting of multiple phases was prepared by arc melting which exposes the material to an extreme rate of cooling, while the single-phase material is prepared to slow cooling of the constituents in an Al flux. It is possible that the multiple-phase material actually has a non-equilibrium (defect) structure. This study shows the standard deviations of the y and z parameters for Be(2) are sufficiently small to allow their measurement as a function of pressure. Such a pressure-dependent structural investigation should provide a better understanding of the nature of the 30 kbar transition observed in electrical-resistivity measurements on UBe_{13} (McElfresh, Maple, Willis, Fisk, Thompson & Smith, 1989).

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Structure of Nickel(II) Perbromate Hexahydrate at 296 K

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Abstract. $Ni(BrO_4)_2.6H_2O$, $M_r = 454{\cdot}61$, trigonal, $P\bar{3}$, $a = 7{\cdot}874$ (1), $c = 5{\cdot}423$ (2) Å, $V = 291{\cdot}2$ (1) Å^3, $Z = 1$, $D_x = 2{\cdot}59$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 85{\cdot}36$ cm^{-1}, $F(000) = 222$, $T = 296$ K, $R = 0{\cdot}029$ for 457 unique reflections having $I > 0$. The room-temperature structure is very similar to that reported previously for a sample at 169 K. The water O atoms form a very slightly distorted octahedron about nickel while the perbromate-ion geometry is virtually regular tetrahedral. Both the coordination polyhedron and the perbromate ion were tested and found to behave as rigid bodies. Corrected for rigid-body motion, the Ni—O(2) distance is 2·064 (2) Å and the mean Br—O distance in the perbromate ion is 1·629 (3) Å. A detailed account of the hydrogen bonding is presented. The structure previously

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