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Neutron-diffraction studies of UBe₁₃ and ThBe₁₃

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Neutron-diffraction measurements have been made on polycrystalline samples of UBe₁₃ and ThBe₁₃ at several temperatures between 10 and 250 K. Refinement of the powder patterns using the Rietveld method of profile analysis yields structural parameters in substantial agreement with previous work [space group O_h^c (*Fm3c*); 8 U in 8(*a*); 8 Be(I) in 8(*b*); 96 Be(II) in 96(*i*)]. Values for the (*y,z*) coordinates of the 96 Be(II) are (0.1763, 0.1150) and (0.1745, 0.1129) for UBe₁₃ and ThBe₁₃, respectively. They correspond very closely to those values required for angular snub-cube coordination of the Be(II) around the uranium atoms.

I. INTRODUCTION

The discovery¹ of superconductivity in the heavy-fermion system UBe₁₃ has stimulated new investigations of both the normal and superconducting states of this material. Previous structural studies of the MBe₁₃ (*M* = Ce, Th, U, Zr) intermetallic compounds have been reported by Baenziger and Rundle² and Koehler, Singer, and Coffinberry.³ Qualitative agreement between the observed x-ray and neutron profiles was obtained by use of the parameters known for NaZn₁₃.⁴ In view of the recent interest in UBe₁₃, and the fact that a quantitative detailed analysis of its structure has not yet been performed, we have carried out a detailed structural analysis by Rietveld refinement⁵ of neutron powder data of UBe₁₃ and ThBe₁₃. In addition, our measurements of the UBe₁₃ and ThBe₁₃ powder spectra were made at several temperatures, providing information about the temperature dependence of the lattice constant, positional parameters, and temperature factors.

II. EXPERIMENTAL

Samples of UBe₁₃ and ThBe₁₃ were prepared by use of a method described elsewhere,¹ powdered, and passed

through a sieve with 420- μ m openings. The UBe₁₃ powder was loaded into an aluminum cylinder 1 cm in diameter and 2.5 cm long. This sample holder was placed in a second aluminum can, filled with He gas, sealed, and attached to the cold finger of a Displex refrigerator. The ThBe₁₃ sample was similarly handled, however, a 2.5-cm-diam sample holder was used. The measurements were performed at several temperatures between 10 and 250 K as indicated in Table I. The temperature was regulated to within ± 1 K.

The powder-diffraction measurements were made on a triple-axis spectrometer at the Brookhaven National Laboratory High-Flux Beam Reactor (HFBR) using a bent pyrolytic graphite (PG)(002) monochromator and a bent PG(004) analyzer both set to diffract 14.7 meV neutrons ($\lambda = 2.359$ Å). The horizontal collimation was 40'-open-40'-20' between the reactor and monochromator, the monochromator and sample, the sample and analyzer, and the analyzer and detector, respectively. A PG filter was used before the monochromator to eliminate $\lambda/2$ contamination. Data were taken over a range in scattering angle of 20°–130° encompassing thirteen reflections. A few small ($\ll 1\%$ of the most intense reflection) impurity peaks were observed in the diffraction spectra and could not be identified.

The samples were examined for the presence of large

TABLE I. Profile refinement results.

<i>T</i> (K)	<i>a</i> ₀ (Å)	<i>y</i>	<i>z</i>	<i>B</i> _U	<i>B</i> _{Be(I)}	<i>B</i> _{Be(II)}	<i>R</i> _I ^a	<i>R</i> _{wp} ^a	<i>R</i> _E ^a
UBe ₁₃									
10	10.248 87(2) ^b	0.1763(1) ^b	0.1150(1)	0.7(1)	0.1(1)	1.1(1)	2.06	5.90	3.83
50	10.249 87(3)	0.1763(1)	0.1148(1)	0.3(1)	0.2(1)	0.8(1)	1.54	6.38	3.83
100	10.250 39(2)	0.1761(1)	0.1150(1)	0.7(1)	0.2(1)	1.1(1)	1.23	5.84	3.81
175	10.254 05(3)	0.1765(1)	0.1152(1)	0.9(1)	0.8(1)	1.4(1)	1.12	6.61	3.96
250	10.260 19(3)	0.1763(1)	0.1150(1)	0.9(1)	0.4(1)	1.3(1)	1.41	6.67	3.86
ThBe ₁₃									
10	10.410 05(3)	0.1745(1)	0.1129(1)	0.2(1)	0.6(1)	1.0(1)	3.41	6.52	2.3
100	10.410 55(3)	0.1747(1)	0.1130(1)	0.2(1)	0.4(1)	0.8(1)	4.27	7.12	2.31
250 ^c	10.417 27(4)	0.1751(2)	0.1175(2)	3.37	5.35	2.13

^aSee Ref. 5 for definitions.

^bNumbers in parenthesis refer to the estimated standard deviation referred to the last digit.

^cIncomplete data set.

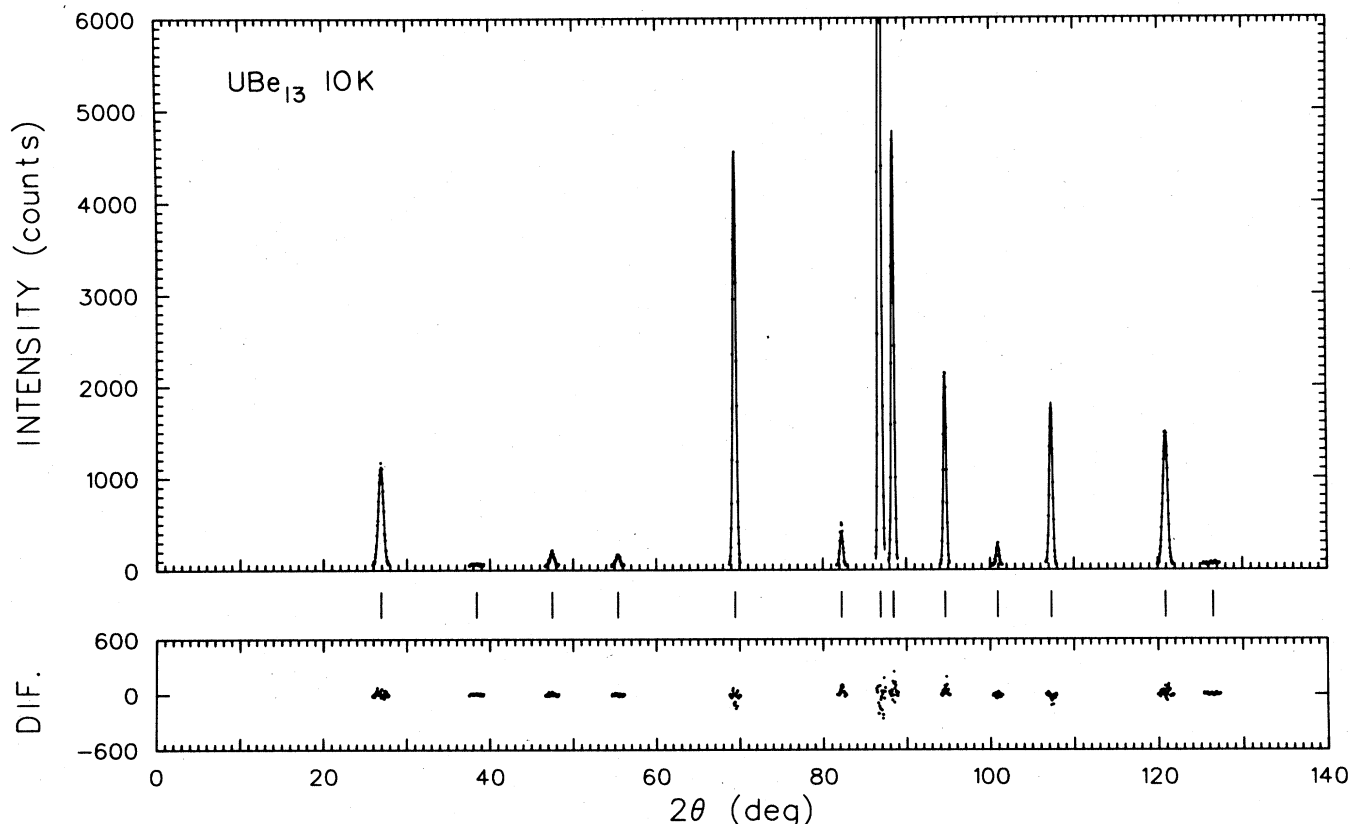


FIG. 1. Fit to the UBe_{13} powder pattern at $T=10$ K and residuals of the fit. The short vertical lines indicate allowed reflections.

grains by setting the spectrometer to the correct scattering angle for the (531) reflection and rotating the sample. Variations in intensity of approximately 30% indicated the presence of grains in the UBe_{13} sample, while no significant intensity variations were noted for the ThBe_{13} powder. In order to minimize these effects, powder patterns for UBe_{13} were recorded while the sample table was rotated between -45° and $+45^\circ$ at each data point. The absorption of both samples was determined by measuring the transmitted in-

tensity, enabling self-shielding corrections⁶ to the temperature factors to be made.

The results of the refinement are summarized in Table I. In the refinement procedure, two positional structural parameters [the Be(II) atoms $0,y,z$], the lattice constant a_0 , and three isotropic temperature factors (B_M , $B_{\text{Be(I)}}$, $B_{\text{Be(II)}}$), were optimized. For details of the Rietveld refinement procedure, the reader is directed to Ref. 5. The data, fit, and residuals of the UBe_{13} ($T=10$ K) profile are shown in Fig. 1. In all cases reasonable fits to the observed data were obtained. The three R -factor entries in Table I are a measure of the goodness of fit of the calculated profile to the data, and are described in Ref. 5.

As indicated in Table I, the UBe_{13} lattice parameter increases smoothly from about 10.2489 Å at 10 K to 10.2602 Å at 250 K. Comparing the lattice constants of UBe_{13} and ThBe_{13} at 10 and 250 K, we find that the thermal expansion of the UBe_{13} lattice is nearly twice as large. The positional coordinates $(0,y,z)$ of the Be(II) atoms are temperature independent throughout the range investigated. Based on these values for a_0 , y , and z , Table II lists the calculated nearest-neighbor distances in UBe_{13} .

TABLE II. Nearest-neighbor distances in UBe_{13} at 10 K.

Bond to atom	Number of bonds	d (Å)
A. Bonds involving U		
Be(II) $(0,y,z)$	24	3.01
B. Bonds involving Be(I)		
Be(II) $(0,y,z)$	12	2.16
C. Bonds involving Be(II)		
Be(I) $(0,0,0)$	1	2.16
U $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	2	3.01
Be(II) $(0,z, \frac{1}{2}-y)$	2	2.23
Be(II) $(z, 0,y)$	4	2.25
Be(II) $(0,y,\bar{z})$	1	2.36
Be(II) $(z, \frac{1}{2}-y, 0)$	2	2.25

III. DISCUSSION

Our values for a_0 , y , and z agree substantially with those of previous investigations.^{2,3} The structure of the MBe_{13} ($M=\text{U, Th}$) compounds belongs to the cubic NaZn_{13} -type

family with space group O_h^5 ($Fm3c$) with

$$U\ 8(a): \pm \frac{1}{4}, \frac{1}{4}, \frac{1}{4},$$

$$Be(I)\ 8(b): 0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2},$$

$$Be(II)\ 96(i): \pm O, y, z; \text{ etc.}$$

The average values for (y, z) in UBe_{13} and $ThBe_{13}$ were determined to be (0.1763, 0.1150) and (0.1745, 0.1129), respectively. The structure of the $NaZn_{13}$ -type compounds has been discussed in detail by Shoemaker *et al.*⁷ The eight U ions and eight Be(I) atoms form a CsCl-type lattice, each U being coordinated by 24 Be(II) atoms at the corners of a nearly regular snub cube. The snub cube may be visualized by snipping off the eight corners of a cube with a U ion at the center. The Be(I) sites are surrounded by 12 Be(II) atoms on a nearly regular icosahedron. However, the conditions for regular snub-cube coordination ($y = 0.1761$, $z = 0.1141$) and icosahedral coordination ($y = 1.618z$) are incompatible. Figure 2 is a parameter plot⁷ which graphically displays the constraints for regular snub-cube and regular icosahedral coordination. Also plotted are the values of y and z determined for UBe_{13} and $ThBe_{13}$ in this work, along with those determined for $CeBe_{13}$,² $NaZn_{13}$,⁷ and KCd_{13} (Ref. 8) measured in previous studies. Uncertainties, where known, are indicated by the radii of circles drawn around the points. While the positional parameters derived for the $NaZn_{13}$ and KCd_{13} compounds differ from those appropriate to either snub-cube or icosahedral regularity, y and z for UBe_{13} correspond closely to the values required for regular snub-cube coordination of the U ions by the Be(II) atoms. These values are also close to those used by Bucher *et al.*⁹ in their crystal-field calculations based on the $CeBe_{13}$ positional parameters. In general, it appears that in the MBe_{13} compounds, the near-neighbor environment of the M ions is more regular than that found in other compounds in the $NaZn_{13}$ -type structural family.

Table I also lists the values obtained for the isotropic temperature factors (B) for each site in the structure, corrected for shielding (absorption) effects for each sample.⁶ Here, the thermal parameter $B = 8\pi^2 \langle u_{ij}^2 \rangle$, where $\langle u_{ij}^2 \rangle$ is the mean-square displacement along the scattering vector. There is clearly some scatter in the values in excess of the estimated standard deviations probably caused by systematic effects. Nevertheless, we can make some qualitative conclusions. First, we note that $B_{Be(II)}$ is consistently larger than $B_{Be(I)}$ for both UBe_{13} and $ThBe_{13}$, and no significant temperature dependence for these factors is observed. This indicates that there is substantially greater static disorder on the Be(II) sites than on the Be(I) sites. Refinements in which anisotropic temperature factors were included, or the

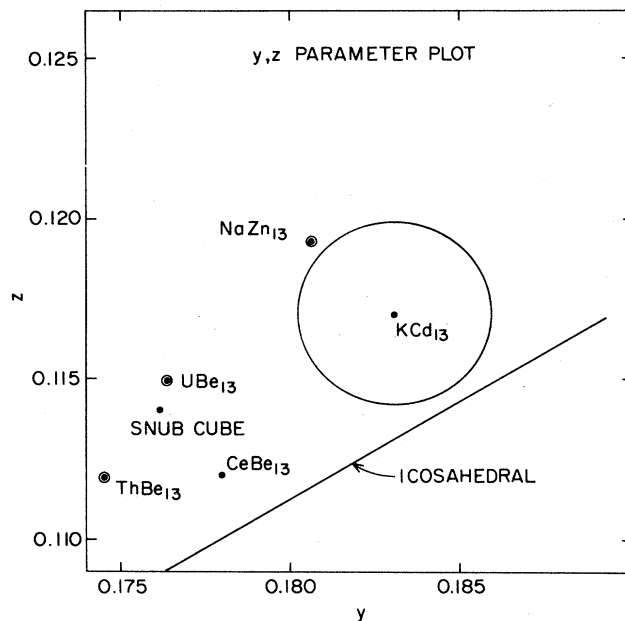


FIG. 2. Parameter plot of y and z for compounds with the $NaZn_{13}$ family-type structure. Radii around points indicate calculated errors.

Be(II) site occupancy was varied, gave no significant change. Second, it can be seen from Table I that B_U is larger than B_{Th} at 10 and 100 K. Recently, Overhauser and Appel¹⁰ have proposed that if there is significant hybridization between the localized f and band-like s electrons, the U-Be spring constant should be substantially smaller than the Th-Be spring constant. This should result in an effective Debye temperature which is smaller for U in UBe_{13} than for Th in $ThBe_{13}$, and is therefore qualitatively consistent with our observation. This point can be checked much more accurately with x rays, and measurements of the Debye-Waller factor for the U and Th atoms are currently underway.

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