Title
NEUTRON-DIFFRACTION STUDIES OF UBE13 AND THBE13

Permalink
https://escholarship.org/uc/item/2st4r4r6

Journal
PHYSICAL REVIEW B, 32(9)

ISSN
0163-1829

Authors
GOLDMAN, AI
SHAPIRO, SM
COX, DE
et al.

Publication Date
1985

DOI
10.1103/PhysRevB.32.6042

License
CC BY 4.0

Peer reviewed
Neutron-diffraction studies of UBe$_{13}$ and ThBe$_{13}$

A. I. Goldman, S. M. Shapiro, and D. E. Cox

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

J. L. Smith and Z. Fisk

Materials Science and Technology Division, Los Alamos National Laboratory,

Los Alamos, New Mexico 87545

(Received 25 June 1985)

Neutron-diffraction measurements have been made on polycrystalline samples of UBe$_{13}$ and ThBe$_{13}$ 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 $O_h^6$ ($Fm\bar{3}c$); 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 UBe$_{13}$ and ThBe$_{13}$, 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 discovery$^1$ of superconductivity in the heavy-fermion system UBe$_{13}$ has stimulated new investigations of both the normal and superconducting states of this material. Previous structural studies of the $M$Be$_{13}$ ($M = $ Ce, Th, U, Zr) intermetallic compounds have been reported by Baenziger and Rundle$^2$ 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 NaZn$_{13}$.$^4$

In view of the recent interest in UBe$_{13}$, 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 refinement$^5$ of neutron powder data of UBe$_{13}$ and ThBe$_{13}$. In addition, our measurements of the UBe$_{13}$ and ThBe$_{13}$ 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 UBe$_{13}$ and ThBe$_{13}$ were prepared by use of a method described elsewhere,$^1$ powdered, and passed through a sieve with 420-μm openings. The UBe$_{13}$ 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 ThBe$_{13}$ 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 ($<<1\%$ 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.**

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$a_0$ (Å)</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_U$</th>
<th>$B_{Be(I)}$</th>
<th>$B_{Be(II)}$</th>
<th>$R_I$</th>
<th>$R_{wp}$</th>
<th>$R_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBe$_{13}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10.24887(2)$^b$</td>
<td>0.1763(1)$^b$</td>
<td>0.1150(1)</td>
<td>0.7(1)</td>
<td>0.1(1)</td>
<td>1.1(1)</td>
<td>2.06</td>
<td>5.90</td>
<td>3.83</td>
</tr>
<tr>
<td>50</td>
<td>10.24987(3)</td>
<td>0.1763(1)</td>
<td>0.1148(1)</td>
<td>0.3(1)</td>
<td>0.2(1)</td>
<td>0.8(1)</td>
<td>1.54</td>
<td>6.38</td>
<td>3.83</td>
</tr>
<tr>
<td>100</td>
<td>10.25039(2)</td>
<td>0.1761(1)</td>
<td>0.1150(1)</td>
<td>0.7(1)</td>
<td>0.2(1)</td>
<td>1.1(1)</td>
<td>1.23</td>
<td>5.84</td>
<td>3.81</td>
</tr>
<tr>
<td>175</td>
<td>10.25405(3)</td>
<td>0.1765(1)</td>
<td>0.1152(1)</td>
<td>0.9(1)</td>
<td>0.8(1)</td>
<td>1.4(1)</td>
<td>1.12</td>
<td>6.61</td>
<td>3.96</td>
</tr>
<tr>
<td>250</td>
<td>10.26019(3)</td>
<td>0.1763(1)</td>
<td>0.1150(1)</td>
<td>0.9(1)</td>
<td>0.4(1)</td>
<td>1.3(1)</td>
<td>1.41</td>
<td>6.67</td>
<td>3.86</td>
</tr>
<tr>
<td>ThBe$_{13}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10.41005(3)</td>
<td>0.1745(1)</td>
<td>0.1129(1)</td>
<td>0.2(1)</td>
<td>0.6(1)</td>
<td>1.0(1)</td>
<td>3.41</td>
<td>6.52</td>
<td>2.3</td>
</tr>
<tr>
<td>100</td>
<td>10.41055(3)</td>
<td>0.1747(1)</td>
<td>0.1130(1)</td>
<td>0.2(1)</td>
<td>0.4(1)</td>
<td>0.8(1)</td>
<td>4.27</td>
<td>7.12</td>
<td>2.31</td>
</tr>
<tr>
<td>250$^c$</td>
<td>10.41727(4)</td>
<td>0.1751(2)</td>
<td>0.1175(2)</td>
<td></td>
<td></td>
<td></td>
<td>3.37</td>
<td>5.35</td>
<td>2.13</td>
</tr>
</tbody>
</table>

$^a$See Ref. 5 for definitions.

$^b$Numbers in parenthesis refer to the estimated standard deviation referred to the last digit.

$^c$Incomplete data set.
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 $-45^\circ$ and $+45^\circ$ at each data point. The absorption of both samples was determined by measuring the transmitted intensity, enabling self-shielding corrections 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 ($B_M$, $B_{Be(I)}$, $B_{Be(II)}$), 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$_{13}$.

### III. DISCUSSION

Our values for $a_0$, $y$, and $z$ agree substantially with those of previous investigations. The structure of the MBe$_{13}$ ($M = U, \text{Th}$) compounds belongs to the cubic NaZn$_{13}$-type
family with space group $O_h^k (Fm\overline{3}c)$ with

\[
U \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \\
Be(II) 8(b): 0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2},
\]

Be(II) 96(e): $\pm O, y, z$ etc.

The average values for $(y, z)$ in UBe$_3$ and ThBe$_3$ 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.\footnote{D. P. Shoemaker, R. E. Marsh, F. J. Ewing, and L. Pauling, Acta Crystallogr. 6, 637 (1952).} 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 can 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 ($y = 1.6132$) are incommensurable. Figure 2 is a parameter plot 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$_3$ and ThBe$_3$ in this work, along with those determined for CeBe$_3$.\footnote{E. Bucher, J. P. Maita, G. W. Hull, R. C. Fulton, and A. S. Cooper, Phys. Rev. B11, 440 (1975).} NaZn$_{13}$,\footnote{A. W. Overhauser and J. Appel, Phys. Rev. B 31, 193 (1985).} 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$_3$ 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.\footnote{A. W. Hewat, Acta Crystallogr. A 35, 248 (1979).} in their crystal-field calculations based on the CeBe$_3$ positional parameters. In general, it appears that in the MBe$_3$ 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.\footnote{H. M. Rietveld, J. Appl. Cryst. 2, 65 (1969); A. W. Hewat, United Kingdom Atomic Energy Authority Research Group Report No. RRL73-1897, 1973 (unpublished).} Here, the thermal parameter $B = 8\pi^2(u^2)$, where $\langle u^2 \rangle$ 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 $B_{\text{Be(II)}}$ is consistently larger than $B_{\text{Be(I)}}$ for both UBe$_3$ and ThBe$_3$, 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

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Parameter plot of $y$ and $z$ for compounds with the NaZn$_{13}$ family-type structure. Radii around points indicate calculated errors.}
\end{figure}

Be(II) site occupancy was varied, gave no significant change. Second, it can be seen from Table I that $B_{\text{U}}$ is larger than $B_{\text{Th}}$ at 10 and 100 K. Recently, Overhauser and Appel\cite{Overhauser1985} 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$_3$ than for Th in ThBe$_3$, 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.

\section*{Acknowledgment}

The work at Brookhaven National Laboratory is supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016, and that at Los Alamos National Laboratory is supported also by the U.S. Department of Energy.

\begin{thebibliography}{9}
\bibitem{Zintl1938} E. Zintl and W. Haucke, Z. Electrochem. 44, 104 (1938).
\end{thebibliography}