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Citation	Physical Review Materials, 2(5), 053603 <a href="https://doi.org/10.1103/PhysRevMaterials.2.053603">https://doi.org/10.1103/PhysRevMaterials.2.053603</a>
Issue Date	2018-05-09
Doc URL	<a href="http://hdl.handle.net/2115/71444">http://hdl.handle.net/2115/71444</a>
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Type	article
File Information	PhysRevMaterials.2.053603.pdf



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## Low-temperature x-ray crystal structure analysis of the cage-structured compounds $M\text{Be}_{13}$ ( $M = \text{La}, \text{Sm}, \text{and U}$ )

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(Received 10 November 2017; revised manuscript received 2 April 2018; published 9 May 2018)

The beryllides  $M\text{Be}_{13}$  ( $M = \text{rare earths and actinides}$ ) crystallize in a  $\text{NaZn}_{13}$ -type cubic structure, which can be categorized as a cage-structured compound. In this study, powder x-ray diffraction measurements have been performed on  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ , and  $\text{UBe}_{13}$  in the temperature range between 7 and 300 K in order to investigate their crystallographic characteristics systematically. They keep the  $\text{NaZn}_{13}$ -type cubic structure down to the lowest temperature. We estimated their Debye temperature to be 600–750 K from analyses of the temperature dependence of a lattice parameter, being in good agreement with the values reported previously. Rietveld refinements on the obtained powder patterns revealed that the  $M$  atom in the  $8a$  site is located in an almost ideal snub cube formed by 24  $\text{Be}^{\text{II}}$  atoms in the  $96i$  site, whose caged structure is unchanged even at the low temperatures. In addition, it is argued from the temperature variation of an isotropic mean-square displacement parameter that the  $M\text{Be}_{13}$  compounds commonly have a low-energy phonon mode, which can be described by a model assuming an Einstein oscillation of the  $M$  atom with a characteristic temperature of  $\sim 160$  K.

DOI: [10.1103/PhysRevMaterials.2.053603](https://doi.org/10.1103/PhysRevMaterials.2.053603)

### I. INTRODUCTION

For the past several decades, intermetallic compounds with a caged structure have been intensively studied as potential candidates for thermoelectric conversion applications [1–3]. In the research field of the strongly correlated electron systems, cage-structured compounds, e.g., filled skutterudites, clathrates,  $\beta$ -pyroclorites, hexaborides, and  $\text{Al}_{10}\text{V}$ , have attracted much attention because of their novel phenomena, such as higher-rank multipole ordering in  $\text{PrRu}_4\text{P}_{12}$  [4], a magnetic-field-robust heavy-fermion (HF) state in  $\text{SmOs}_4\text{Sb}_{12}$  [5], and a low-energy phonon mode associated with local vibration of a guest atom with a large amplitude in an oversized host cage, so-called rattling [2,6–10]. Among them, the rattling has been considered to be related with several intriguing phenomena via interaction with conduction electrons, for example, a rattling-induced superconductivity [11], unusual temperature dependence of the electrical resistivity [12], and a magnetic-field-insensitive HF state due to the multilevel Kondo effect [13]. In contrast to the previous expectations, it has recently been claimed from neutron spectroscopy experiments that a picture of a freely rattling guest atom in a host cage is not applicable in the case of filled  $\text{Fe}_4\text{Sb}_{12}$  skutterudites [14]. Thus the issue of rattling is still controversial. To verify the underlying concept of rattling itself, it is highly necessary to examine crystallographic characteristics at low temperatures for several cage-structured systems.

The beryllide  $M\text{Be}_{13}$  can also be categorized as a cage-structured compound, where  $M$  is a rare earth or an actinide. They crystallize in a  $\text{NaZn}_{13}$ -type cubic structure with the space group  $Fm\bar{3}c$  (No. 226,  $O_h^6$ ), where the unit cell contains  $M$  atoms in the  $8a$  site,  $\text{Be}^{\text{I}}$  atoms on the  $8b$  site, and  $\text{Be}^{\text{II}}$  atoms in the  $96i$  site [15–17]. The  $M$  atoms are surrounded by 24  $\text{Be}^{\text{II}}$  atoms, nearly forming an ideal snub cube, whereas the  $\text{Be}^{\text{I}}$  atoms are surrounded by 12  $\text{Be}^{\text{II}}$  atoms, forming an icosahedron cage, as shown in Fig. 1.

For the phonon physics in  $M\text{Be}_{13}$ , previous specific-heat and inelastic neutron scattering (INS) measurements revealed that  $\text{UBe}_{13}$ ,  $\text{ThBe}_{13}$ , and possibly  $\text{LaBe}_{13}$  have a low-energy phonon mode, which can be described by an Einstein mode with characteristic temperatures of  $\theta_E = 151, 157, \text{ and } 177$  K, respectively [18,19]. To discuss a possibility of an influence of the low-energy phonon mode on novel phenomena in the  $M\text{Be}_{13}$  system, such as unconventional HF superconductivity and non-Fermi-liquid behavior in  $\text{UBe}_{13}$  [20,21] and an intermediate valence state due to the strong  $c$ - $f$  hybridization in  $\text{CeBe}_{13}$  [22], it is necessary to elucidate characteristics of the low-energy phonon mode. It has been suggested that the  $M$  atom behaves like an Einstein oscillator in  $\text{UBe}_{13}$  and  $\text{ThBe}_{13}$  [18], while other characteristics of the low-energy phonon mode in the present system have been veiled: for example, coupling between the guest ions and the host lattice, form of the potential energy (harmonic or anharmonic), and size effects of the cage. Systematic crystallographic studies on the low-energy phonon mode for the  $M\text{Be}_{13}$  series would provide important information to unveil the universal nature of the phonon properties in  $M\text{Be}_{13}$  with unique cagelike structures.

A low-temperature systematic investigation of crystal structure is also crucial to unveil the physical ground-state properties, such as a gap symmetry of the unconventional superconductivity in  $\text{UBe}_{13}$  [23] and crystalline-electric-field effects

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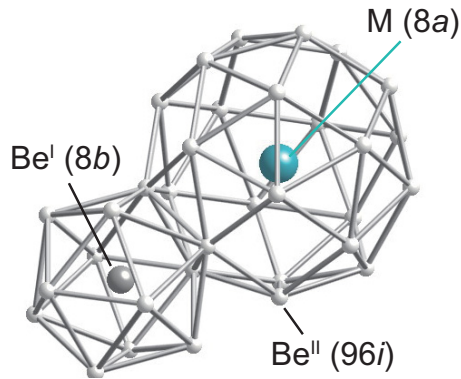


FIG. 1. Cagelike structures of  $MBe_{13}$ . The  $M$  and  $Be^I$  atoms are placed into an almost ideal snub cube and an icosahedron formed by the  $Be^{II}$  atoms, respectively.

in all the magnetic  $MBe_{13}$  compounds, both of which may be affected by some crystal distortion. A lattice parameter  $a$  at room temperature (RT) has already been reported in all the  $MBe_{13}$  compounds [15,24], while the low-temperature data are limited in some  $MBe_{13}$  compounds [25,26]. The fractional  $(0, y, z)$  coordinates of the  $Be^{II}$  site at RT have been determined in several  $MBe_{13}$  ( $M = La, Ce, Dy, Th, \text{ and } U$ ) [19,26,27], whereas their low-temperature values have been determined only in  $UBe_{13}$  and  $ThBe_{13}$  [26]. In addition, studies on an atomic displacement parameter for  $MBe_{13}$ , which can be a useful guide to understand phonon properties [2,7], have remained untouched even at RT except for  $UBe_{13}$  and  $ThBe_{13}$  [26].

In this study, we investigated structure parameters and phonon properties of a superconductor  $LaBe_{13}$  with a superconducting transition temperature of  $\sim 0.6$  K [19], a possible helical magnet  $SmBe_{13}$  with a magnetic transition temperature of  $T_M = 8.3$  K [15,28,29], and an unconventional HF superconductor  $UBe_{13}$  [20] by x-ray diffraction (XRD) measurements in temperatures of down to 7 K. The results of the XRD measurements and Rietveld analyses are presented in Sec. III: the temperature dependence of the lattice parameter in subsection A, the fractional  $(0, y, z)$  coordinates in subsection B, and isotropic mean-square displacement parameters in subsection C.

## II. EXPERIMENT

Single crystals of  $LaBe_{13}$ ,  $SmBe_{13}$ , and  $UBe_{13}$  were grown by an Al-flux method. The constitute materials were La with 99.9% purity, Sm with 99.9% purity, U with 99.5% purity, Be with 99% purity, and Al with 99.99% purity. Each  $M$  element was placed in an  $Al_2O_3$  crucible with Be and Al at an atomic ratio of  $La:Be:Al = 1:13:35$ ,  $Sm:Be:Al = 1:13:30$ , and  $U:Be:Al = 1:13:40$ , and sealed in a quartz tube filled with ultrahigh-purity Ar gas of 150 mmHg. The sealed tube was kept at  $1050^\circ C$  for 1 week and then cooled at a rate of  $2^\circ C/h$ . The Al flux was spun off in a centrifuge and then removed by NaOH solution. The obtained single crystals were annealed for 2 weeks at  $700^\circ C$ . The annealed samples were ground into fine

powders in the ethyl alcohol and then put in a copper holder for XRD.

The XRD measurements were performed by a conventional powder x-ray diffractometer (Rint 2000, Rigaku) using  $Cu K\alpha_1$  and  $K\alpha_2$  radiation in the angle range of  $15^\circ < 2\theta < 157^\circ$ . A Gifford-McMahon refrigerator was used for the low-temperature measurements down to 7 K. Rietveld refinement on the powder XRD data was carried out using the RIETAN-FP program [30].

## III. RESULT AND DISCUSSION

### A. Lattice parameters

Figure 2 shows the powder XRD patterns of  $SmBe_{13}$  at (a) 300 and (b) 7 K. The obtained XRD patterns can be well fitted assuming the  $NaZn_{13}$ -type cubic structure. In addition, we do not observe any peaks associated with impurity phases except for reflections from the copper holder. We note that any residual peaks are smaller than 0.3% of the principal reflection. In the present XRD measurements, we succeeded in observing weak signals, which originate from only the  $Be^{II}$  atoms, for example (531) reflection, promising determination of the fractional coordinates of the  $Be^{II}$  atom. In addition, there is no obvious difference in the XRD patterns between 300 and 7 K except for a shift of the peak positions on the  $2\theta$  axis due to a change in the lattice parameter. Similar results were obtained in  $LaBe_{13}$  and  $UBe_{13}$  (not shown), indicating absence of a structural transition in this temperature region. The lattice parameter  $a$  was determined from the obtained

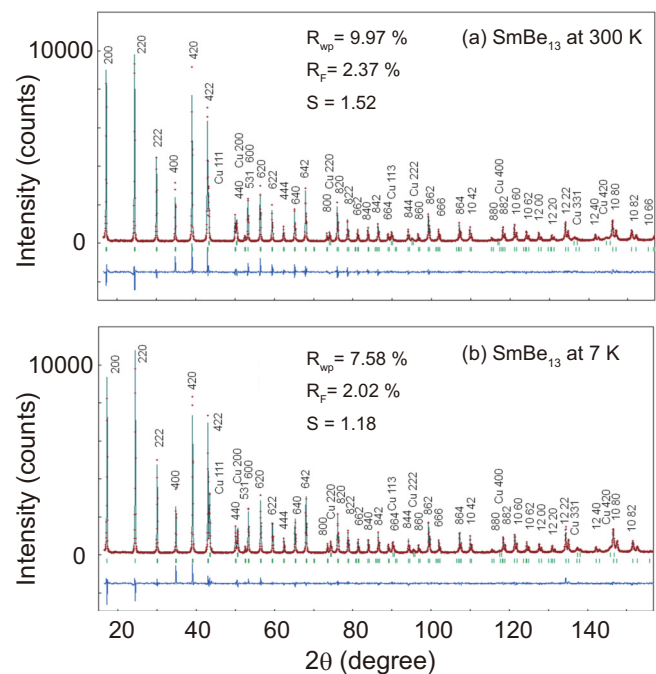


FIG. 2. Observed powder XRD patterns of  $SmBe_{13}$  (cross symbols) and calculated profiles (solid lines) at (a) 300 and (b) 7 K. The green vertical bars below the XRD patterns indicate the calculated peak positions. The difference between the observed and calculated intensities is indicated by the blue line at the bottom of each figure.

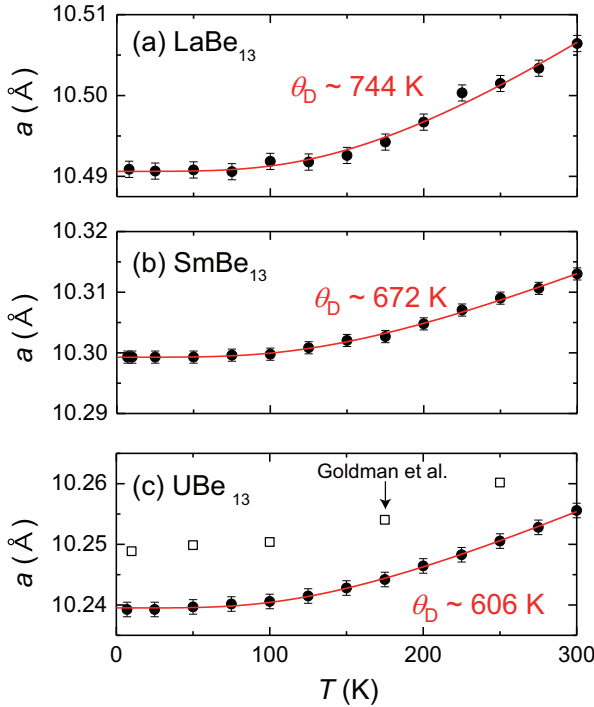


FIG. 3. Temperature dependence of the lattice parameter  $a(T)$  for (a)  $\text{LaBe}_{13}$ , (b)  $\text{SmBe}_{13}$ , and (c)  $\text{UBe}_{13}$ . The solid lines represent the fitting curves based on the Debye-Grüneisen approximation, as described in the text. The open symbols in Fig. 3(c) are the data reported previously [26].

XRD peaks at high  $2\theta$  angles ( $2\theta > 110^\circ$ ) using the Bragg's law. The obtained lattice parameter at 300 K and at the lowest temperature for  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ , and  $\text{UBe}_{13}$  are shown in Table I, which are approximately consistent with those reported previously [15,16].

Figure 3 shows the temperature dependence of the lattice parameter  $a(T)$  for (a)  $\text{LaBe}_{13}$ , (b)  $\text{SmBe}_{13}$ , and (c)  $\text{UBe}_{13}$ . For all three compounds investigated here, the lattice parameter decreases as the temperature is lowered, and levels off below  $\sim 100$  K. The data of  $\text{UBe}_{13}$  reported previously are also indicated as the open symbols in Fig. 3(c) [26]. Although the lattice parameter of our  $\text{UBe}_{13}$  sample is slightly smaller than that reported in Ref. [26], the observed temperature variation is in good agreement with the previous result. Note that there is no anomaly in the  $a(T)$  curve near  $T_M$  of  $\text{SmBe}_{13}$  within the experimental accuracy. From almost linear temperature dependence in the  $a(T)$  curves above  $\sim 150$  K, we estimated a thermal expansion coefficient  $\alpha$  ( $\equiv 1/a da/dT$ ). The estimated  $\alpha$  values at 300 K are  $8.8 \times 10^{-6}$ ,  $7.1 \times 10^{-6}$ , and  $8.3 \times 10^{-6} \text{ K}^{-1}$  for  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ , and  $\text{UBe}_{13}$ , respectively, as summarized in Table II. Similar  $a(T)$  has also been reported in  $\text{YBe}_{13}$ ,  $\text{PrBe}_{13}$ ,  $\text{LuBe}_{13}$ , and  $\text{ThBe}_{13}$ , where  $\alpha$  can be estimated to be  $(7\text{--}9) \times 10^{-6} \text{ K}^{-1}$  [25]. It is revealed that  $\alpha$  above  $\sim 150$  K in the  $M\text{Be}_{13}$  system is almost independent of the  $M$  atom.

To estimate a Debye temperature  $\theta_D$ , the  $a(T)$  curves were analyzed using the Debye-Grüneisen approximation [31]

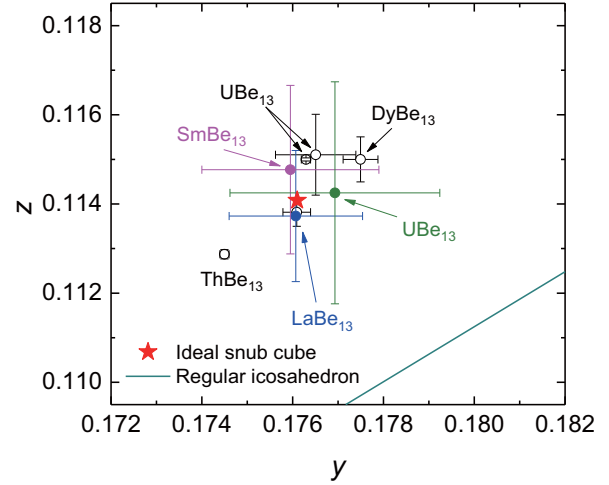


FIG. 4. Parameter plot of  $y$  and  $z$  at RT for several  $M\text{Be}_{13}$  compounds ( $M = \text{La}, \text{Sm}, \text{Dy}, \text{Th}, \text{and U}$ ). The closed and open circle symbols indicate the data obtained from the present and previous studies [26,27], respectively. The fractional coordinates of the  $\text{Be}^{\text{II}}$  atom for  $M\text{Be}_{13}$  are much closer to the ideal snub-cube coordinates (star symbol) than the icosahedron coordinates (solid line).

described by

$$a(T) \cong a_0 \left[ 1 + 3I_a T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3}{\exp(x) - 1} dx \right], \quad (1)$$

$$I_a = \frac{k_B G}{B V_0}, \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $G$  is the Grüneisen parameter,  $B$  is the bulk modulus, and  $a_0$  and  $V_0$  are a lattice parameter and volume of unit cell at absolute zero, respectively. The obtained fitting parameters are  $(\theta_D, a_0, I_a) = (744 \text{ K}, 10.491 \text{ \AA}, 1.4 \times 10^{-5})$  for  $\text{LaBe}_{13}$ ,  $(672 \text{ K}, 10.299 \text{ \AA}, 1.1 \times 10^{-5})$  for  $\text{SmBe}_{13}$ , and  $(606 \text{ K}, 10.240 \text{ \AA}, 1.2 \times 10^{-5})$  for  $\text{UBe}_{13}$ . The obtained  $\theta_D$  values are listed in Table II along with the previously reported values of  $\theta_D$  for  $\text{LaBe}_{13}$  and  $\text{ThBe}_{13}$  [15,19,25]. These results indicate that the  $M\text{Be}_{13}$  systems commonly have relatively high  $\theta_D$  of 600–900 K, although it is necessary to consider an influence of the low-energy phonon mode for more proper discussion.

## B. Fractional ( $0, y, z$ ) coordinates of the $\text{Be}^{\text{II}}$ site

We next show the Rietveld analyses of the obtained XRD patterns assuming the  $\text{NaZn}_{13}$ -type cubic structure. The calculated profiles for  $\text{SmBe}_{13}$  can be seen in Figs. 2(a) and 2(b). Here, the lattice parameter was fixed to the value determined by the analysis of the Bragg's peak scan for the higher angle spectrum. The obtained  $y$  and  $z$  parameters in the fractional coordinates of the  $\text{Be}^{\text{II}}$  site and the typical reliability factors ( $R_{\text{wp}}$ ,  $R_F$ , and  $S$ ) are shown in Table I. Figure 4 shows the  $y$  and  $z$  parameters of the  $\text{Be}^{\text{II}}$  site at RT for several  $M\text{Be}_{13}$  compounds:  $M = \text{La}, \text{Sm}, \text{Dy}, \text{Th}, \text{and U}$  [26,27]. The star

TABLE I. Lattice parameter  $a$ , fractional  $(0, y, z)$  coordinates of the  $\text{Be}^{\text{II}}$  atom, typical reliability factors, i.e.,  $R_{\text{wp}}$ ,  $R_{\text{F}}$ , and  $S$ , in the Rietveld analysis for  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ , and  $\text{UBe}_{13}$  at 300 K and the lowest temperature (8 K for  $\text{LaBe}_{13}$  and 7 K for  $\text{SmBe}_{13}$  and  $\text{UBe}_{13}$ ). The previously reported data are also listed for comparison in this table [15,16,26].

	$\text{LaBe}_{13}$		$\text{SmBe}_{13}$		$\text{UBe}_{13}$	
	300 K	8 K	300 K	7 K	300 K	7 K
$a(\text{\AA})$	10.506(3) 10.451 <sup>a</sup>	10.491(3)	10.313(1) 10.304 <sup>a</sup>	10.299(1)	10.256(1) 10.257 <sup>a</sup> 10.268(2) <sup>b</sup>	10.239(1)
$y$	0.1761(15)	0.1765(13)	0.1760(20)	0.1753(14)	0.1769(23) 0.1763(1) <sup>c</sup>	0.1765(21) 0.1763(1) <sup>d</sup>
$z$	0.1137(15)	0.1142(13)	0.1148(20)	0.1133(15)	0.1143(25) 0.1150(1) <sup>c</sup>	0.1141(23) 0.1150(1) <sup>d</sup>
$R_{\text{wp}}(\%)$	5.66	5.52	9.97	7.58	6.65	7.49
$R_{\text{F}}(\%)$	1.65	1.54	2.37	2.02	1.64	1.79
$S$	1.21	1.18	1.52	1.18	1.48	1.59

<sup>a</sup>Bucher *et al.* [15].

<sup>b</sup>McElfresh *et al.* [16].

<sup>c</sup>Goldman *et al.* at 250 K [26].

<sup>d</sup>Goldman *et al.* 10 K [26].

symbol and the solid line indicate the ideal snub-cube ( $y = 0.17610$ ,  $z = 0.11408$ ) and regular icosahedron [ $y = \frac{1}{2}(1 + \sqrt{5})z$ ] coordinates, respectively. In all the measured  $M\text{Be}_{13}$  compounds, the  $y$  and  $z$  parameters are not close to those in the regular icosahedron coordinates but close to those in the ideal snub-cube coordinates. Furthermore, it is revealed that the  $y$  and  $z$  parameters are almost temperature-independent within the accuracy of the measurements in the present compounds, as shown in Table I, and hence their caged structures keep the almost ideal snub cube even at the low temperatures. This result indicates that the symmetry of a crystalline electric field at the  $M$  site remains unchanged down to 7 K, although the cage size becomes smaller accompanied by the decrease of the lattice parameter upon cooling.

### C. Isotropic mean-square displacement parameter

The isotropic mean-square displacement parameter  $U_{\text{eq}}$  of individual atoms for  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ , and  $\text{UBe}_{13}$  were also determined from the Rietveld analyses. Here, an isotropic atomic displacement parameter is defined as  $8\pi^2 U_{\text{eq}}$ . In general, it is difficult to determine an absolute value of  $U_{\text{eq}}$  precisely, since the precision of  $U_{\text{eq}}$  is strongly influenced by experimental conditions, experimental error, and refinement methods. In the present analyses, for example, the refined  $U_{\text{eq}}$  of the Sm atom for  $\text{SmBe}_{13}$  took on a wide range of value from 0.003 to 0.029 depending on initial parameters at RT. However, once one fixes the initial parameters to some values, the error of the refined  $U_{\text{eq}}$  becomes approximately  $\pm 5\%$ . Therefore, in this study, the temperature dependence of  $U_{\text{eq}}$  [=  $U_{\text{eq}}(T)$ ] was obtained

TABLE II. Thermal expansion coefficient  $\alpha$  at 300 K, Debye temperature  $\theta_{\text{D}}$ , Einstein temperature  $\theta_{\text{E}}$ , and electronic specific-heat coefficient  $\gamma$  for  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ ,  $\text{UBe}_{13}$ , and  $\text{ThBe}_{13}$ .  $\theta_{\text{D}}$  and  $\theta_{\text{E}}$  of the  $M$  atom were estimated from the temperature dependence of  $U_{\text{eq}}$ . The previously reported data are also listed for comparison in this table [15,18–20,25].

		$\alpha$ ( $10^{-6} \text{ K}^{-1}$ )	$\theta_{\text{D}}$ (K)	$\theta_{\text{E}}$ (K)	$\gamma$ ( $\text{mJ mol}^{-1} \text{ K}^{-2}$ )
$\text{LaBe}_{13}$	Bulk	8.8 $\sim 8^{\text{a}}$	744 820 <sup>a,b</sup> 950 <sup>c</sup>	177 <sup>c</sup>	9.1 <sup>c</sup> 8.1 <sup>b</sup>
	La		287	163(15)	
$\text{SmBe}_{13}$	Bulk	7.1	672		
	Sm		270	157(10)	
$\text{UBe}_{13}$	Bulk	8.3	606	151 <sup>d</sup>	$\sim 1000^{\text{e}}$
	U		290	160(20)	
$\text{ThBe}_{13}$	Bulk	7.7 <sup>a</sup>	610 <sup>a</sup>	157 <sup>d</sup>	7.1 <sup>b</sup>
			618 <sup>b</sup>		

<sup>a</sup>Lattice constant (Kappler *et al.*) [25].

<sup>b</sup>Specific heat (Bucher *et al.*) [15].

<sup>c</sup>Specific heat (Hidaka *et al.*) [19].

<sup>d</sup>Inelastic neutron (Renker *et al.*) [18].

<sup>e</sup>Specific heat (Ott *et al.*) [20].

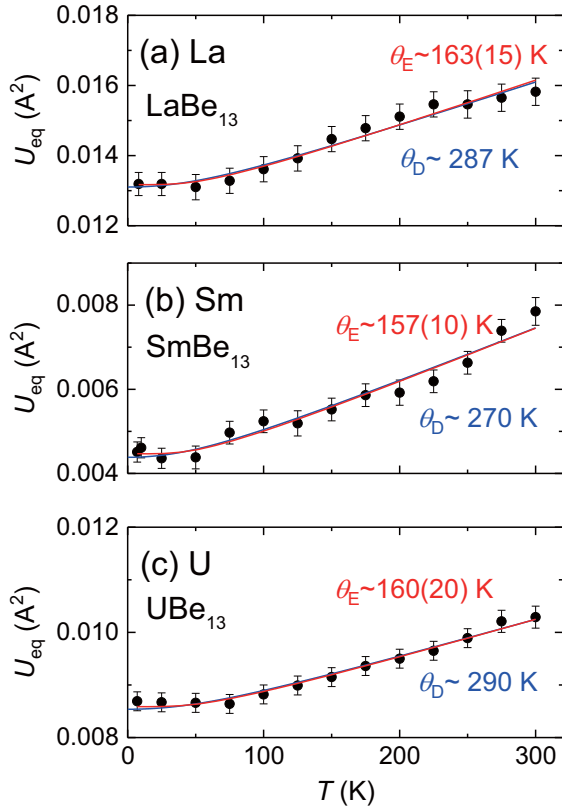


FIG. 5. Temperature dependence of  $U_{\text{eq}}$  of the  $M$  atom for  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ , and  $\text{UBe}_{13}$ : (a)  $M = \text{La}$ , (b)  $\text{Sm}$ , and (c)  $\text{U}$ . The red-solid and blue-solid lines indicate the fitting curves obtained from the calculations based on the Einstein and Debye models, respectively.

by the following procedure: (1) refine  $U_{\text{eq}}$  at 300 K using the Rietveld analysis with some initial parameters, (2) refine  $U_{\text{eq}}$  at 275 K using the initial parameters determined at 300 K, (3) refine  $U_{\text{eq}}$  at 250 K using the initial parameters determined at 275 K, and (4) repeat the process sequentially down to the lowest temperature. Note that we checked that the temperature variation of  $U_{\text{eq}}$  is hardly influenced by the absolute value of  $U_{\text{eq}}$ , i.e., the relative change in  $U_{\text{eq}}(T)$  can be used for analyses to obtain the values of  $\theta_{\text{D}}$  and  $\theta_{\text{E}}$ , as discussed in the next paragraph.

The obtained  $U_{\text{eq}}(T)$  of the  $M$  atom are shown in Fig. 5. Each figure represents (a)  $\text{La}$  of  $\text{LaBe}_{13}$ , (b)  $\text{Sm}$  of  $\text{SmBe}_{13}$ , and (c)  $\text{U}$  of  $\text{UBe}_{13}$ . These experimental results were analyzed using the following two models [2,32]: a Debye model,

$$U_{\text{eq}}^{\text{Deb}}(T) = \frac{3\hbar^2 T}{mk_{\text{B}}\theta_{\text{D}}^2} \left[ \frac{T}{\theta_{\text{D}}} \int_0^{\theta_{\text{D}}/T} \frac{x}{\exp(x) - 1} dx + \frac{\theta_{\text{D}}}{4T} \right] + d^2, \quad (3)$$

and an Einstein model,

$$U_{\text{eq}}^{\text{Ein}}(T) = \frac{\hbar^2}{2mk_{\text{B}}\theta_{\text{E}}} \coth\left(\frac{\theta_{\text{E}}}{2T}\right) + d^2, \quad (4)$$

where  $\hbar$ ,  $m$ , and  $d^2$  are the Planck constant, mass of the atom, and temperature independent disorder term, respectively. The obtained  $\theta_{\text{D}}$  and  $\theta_{\text{E}}$  are listed in Table II, including the results reported previously [18,19].  $U_{\text{eq}}(T)$  of the  $M$  atom decreases

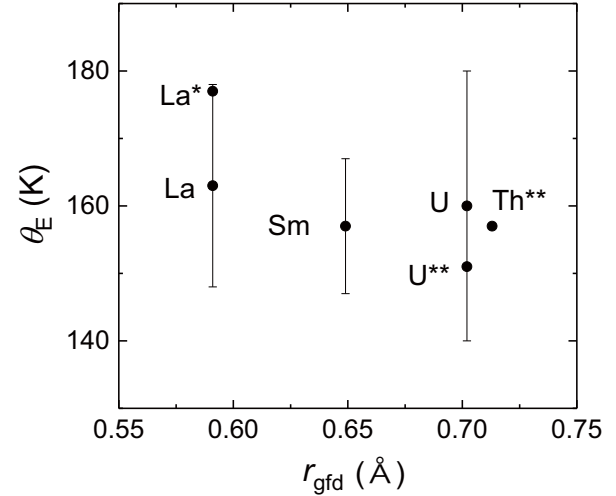


FIG. 6. Einstein temperature  $\theta_{\text{E}}$  vs guest free distance  $r_{\text{gfd}}$  ( $\equiv r_{\text{M-Be}^{\text{II}}} - r_{\text{M}} - r_{\text{Be}^{\text{II}}}$ ) in several  $M\text{Be}_{13}$  compounds, where  $M = \text{La}$ ,  $\text{Sm}$ ,  $\text{Th}$ , and  $\text{U}$ . Some data of  $\theta_{\text{E}}$ , represented as  $\text{La}^*$ ,  $\text{U}^{**}$ , and  $\text{Th}^{**}$ , are taken from literature [18,19].

monotonously with decreasing temperature, as shown in Fig. 5. In the conventional Einstein model, the best fit provides  $\theta_{\text{E}}$  of 163(15), 157(10), and 160(20) K for the  $\text{La}$ ,  $\text{Sm}$ , and  $\text{U}$  atoms, respectively, which are approximately identical to the values estimated from the specific heat ( $C$ ) and INS measurements [18,19]. On the other hand, in the Debye model,  $\theta_{\text{D}}$  were estimated to be  $\sim 287$ ,  $\sim 270$ , and  $\sim 290$  K for the  $\text{La}$ ,  $\text{Sm}$ , and  $\text{U}$  atoms, respectively. These values are less than half compared with those estimated from the  $a(T)$  and  $C(T)$  data [15,19,25]. These results indicate that the Einstein model gives a better description of  $U_{\text{eq}}(T)$  of the  $M$  atom than the Debye model.

In  $U_{\text{eq}}(T)$  of the  $\text{Be}^{\text{I}}$  and  $\text{Be}^{\text{II}}$  atoms, it was quite difficult to perform reliable analyses in both the models due to almost temperature-independent behavior of  $U_{\text{eq}}$  in the investigated temperature range. It is noted that simulated curves based on the Einstein model with  $\theta_{\text{E}}$  of 150 and 170 K obviously deviate from  $U_{\text{eq}}(T)$  of the  $\text{Be}^{\text{I}}$  and  $\text{Be}^{\text{II}}$  atoms (not shown). These findings suggest that the  $M$  atom behaves like an Einstein oscillator with  $\theta_{\text{E}} \sim 160$  K, as pointed out from the previous INS measurements for  $\text{UBe}_{13}$  and  $\text{ThBe}_{13}$  [18], whereas the  $\text{Be}$  atoms form the crystal lattice described by the Debye model.

The low-energy phonon mode, which can be explained by the Einstein phonon with harmonic oscillation, is considered to be a common feature in the  $M\text{Be}_{13}$  systems. It is intriguing that the  $M\text{Be}_{13}$  series appears to have almost the same  $\theta_{\text{E}}$ . In other cage-structured compounds, such as filled skutterudites [6,7],  $\beta$ -pyrochlore oxides [8], and clathrates [2], it has been found that  $\theta_{\text{E}}$  shows a decreasing trend with increasing the free space for guest vibration. This decreasing trend in  $\theta_{\text{E}}$  has been interpreted as follows: larger free space yields shallower guest-ion potential, resulting in a decrease in the energy of the local phonon mode [7]. Here, we test the similar analysis concerning the free space, which has been performed for other cage-structured compounds. Figure 6 shows  $\theta_{\text{E}}$  for  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ ,  $\text{ThBe}_{13}$ , and  $\text{UBe}_{13}$ , plotted against the guest free distance  $r_{\text{gfd}}$  determined at 300 K [18,19]. In this study,  $r_{\text{gfd}}$  is

defined as

$$r_{\text{gfd}} = r_{M-\text{Be}^{\text{II}}} - r_M - r_{\text{Be}^{\text{II}}}, \quad (5)$$

where,  $r_{M-\text{Be}^{\text{II}}}$  is the distance between  $M$  and  $\text{Be}^{\text{II}}$ ,  $r_M$  is the effective ionic radius of  $M$  ( $r_{\text{La}^{3+}} = 1.36 \text{ \AA}$ ,  $r_{\text{Sm}^{3+}} = 1.24 \text{ \AA}$ ,  $r_{\text{Th}^{4+}} = 1.21 \text{ \AA}$ , and  $r_{\text{U}^{4+}} = 1.17 \text{ \AA}$ ) [33], and  $r_{\text{Be}^{\text{II}}}$  is the Be metal-bonding radius ( $= 1.14 \text{ \AA}$ ) [34], respectively. Here, we tentatively used the effective ionic radius for the 12-coordination-number site as  $r_M$  [33], since there is no data for 24-coordination-number sites to our best knowledge. As seen in Fig. 6,  $\theta_E$  is robust to a change in  $r_{\text{gfd}}$  within the range of the error bar, suggesting that the above-mentioned interpretation for other cage-structured compounds is not simply applicable to the  $M\text{Be}_{13}$  systems.

Another key parameter to discuss the low-energy phonon mode is the atomic mass. In the case of the Einstein oscillation,  $k_B\theta_E$  can be rewritten to  $\hbar\omega_E \propto (k/m_E)^{1/2}$ , where  $\omega_E$  is the Einstein frequency,  $k$  is the spring constant, and  $m_E$  is the mass of the Einstein oscillator. Assuming that the  $M\text{Be}_{13}$  compounds have similar values of  $k$ , it is expected that heavier mass of the  $M$  atom ( $= m_M$ ) yields smaller  $\theta_E$ . In this assumption,  $\theta_E$  for  $\text{LaBe}_{13}$  ( $m_{\text{La}} \sim 139$ ) was estimated to be  $\sim 210 \text{ K}$ , when we calculate it from  $\theta_E$  of  $160 \text{ K}$  for  $\text{UBe}_{13}$  ( $m_{\text{U}} \sim 238$ ). This estimated  $\theta_E$  for  $\text{LaBe}_{13}$  deviates from the experimental value of  $\sim 170 \text{ K}$ . This disagreement may be attributed to the present simple assumption that  $k$  has similar values among the  $M\text{Be}_{13}$  compounds, since the value of  $k$  generally depends on  $r_{\text{gfd}}$  and an ionic state of the guest ion. In this context,  $\theta_E$  in the  $M\text{Be}_{13}$  systems might be determined by a combination of several parameters, such as  $r_{\text{gfd}}$ ,  $m_M$ , and possibly electronic states, resulting in similar values of  $\theta_E$ . Furthermore, in this discussion, the low-energy phonon mode was simply treated as the Einstein phonon, which is independent of the Debye phonon, although actual phonon dispersion should be more complicated. Recently, inelastic x-ray scattering measurements in  $\text{SmBe}_{13}$  performed by Tsutsui *et al.* revealed that a phonon dispersion curve of the Sm atom shows a flat part near a zone boundary. The energy of the flat part is approximately  $16 \text{ meV}$ , which is consistent with  $\theta_E$  of  $157(10) \text{ K}$  determined from the present XRD study [35].

Finally we comment on a relationship between the low-energy phonon mode and electronic states of conduction electrons in the  $M\text{Be}_{13}$  systems. It has been theoretically proposed for cage-structured compounds that a possible enhancement

of the quasiparticle mass is caused by the interaction between anharmonic vibration of the guest ion and conduction electrons [13]. The electronic specific-heat coefficient  $\gamma$  for  $M\text{Be}_{13}$  ( $M = \text{La}, \text{Sm}, \text{U}, \text{and Th}$ ) are listed in Table II. The characteristic energy of the low-energy phonon mode appears to have no relation to the value of  $\gamma$ , implying that the HF state for  $\text{UBe}_{13}$  may not originate from the presence of the low-energy phonon mode. However, it has also been suggested that an electron-phonon coupling between the conduction electrons and the low-energy Einstein phonon also plays an important role in formation of the phonon-mediated HF state [36–38]. Therefore, it is necessary to check the strength of the electron—phonon coupling in the  $M\text{Be}_{13}$  systems to reveal the role of the low-energy phonon mode in the HF state for  $\text{UBe}_{13}$ . To deepen our understanding of the low-energy phonon mode in the present systems, further studies, such as a systematic observation of the phonon dispersion and the strength of the electron-phonon coupling, are needed and now in progress.

#### IV. SUMMARY

We measured XRD on powdered  $\text{LaBe}_{13}$ ,  $\text{SmBe}_{13}$ , and  $\text{UBe}_{13}$  at low temperatures in order to investigate their structure parameters and characteristics of the low-energy phonon. The obtained XRD patterns and the Rietveld refinements revealed that the present compounds keep a  $\text{NaZn}_{13}$ -type cubic structure with an almost ideal snub cube formed by 24  $\text{Be}^{\text{II}}$  atoms involving the  $M$  atom even at low temperatures down to  $7 \text{ K}$ . Furthermore, the present study provides crystallographic collateral evidence for the presence of the low-energy phonon modes common to the  $M\text{Be}_{13}$  systems, which can be explained by an Einstein model. It is considered that the rigid  $\text{Be}^{\text{II}}$  framework can be treated as a Debye solid with  $\theta_D$  of  $600\text{--}800 \text{ K}$ , while the  $M$  ions behave like Einstein oscillators with  $\theta_E$  of  $\sim 160 \text{ K}$ . Interestingly, the obtained  $\theta_E$  values in the present systems, including the values reported thus far, appear to be independent of either  $m_M$  or  $r_{\text{gfd}}$  in the snub cube, which is a characteristic feature not found in other cage-structured compounds.

#### ACKNOWLEDGMENTS

The authors thank Dr. S. Tsutsui for fruitful discussions. The present research was supported by JSPS KAKENHI Grants No. JP20224015(S), No. JP25400346(C), No. JP26400342(C), No. JP15KK0146, No. JP15H05882, and No. JP15H05885 (J-Physics).

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- [1] B. C. Sales, D. Mandrus, and R. K. Williams, *Science* **272**, 1325 (1996).
- [2] K. Suekuni, M. A. Avila, K. Umeo, H. Fukuoka, S. Yamanaka, T. Nakagawa, and T. Takabatake, *Phys. Rev. B* **77**, 235119 (2008).
- [3] B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson, and D. Mandrus, *Phys. Rev. B* **63**, 245113 (2001).
- [4] T. Takimoto, *J. Phys. Soc. Jpn.* **75**, 034714 (2006).
- [5] S. Sanada, Y. Aoki, H. Aoki, A. Tsuchiya, D. Kikuchi, H. Sugawara, and H. Sato, *J. Phys. Soc. Jpn.* **74**, 246 (2005).
- [6] K. Matsuhira, Y. Hinatsu, C. Sekine, T. Togashi, H. Maki, I. Shirovani, H. Kitazawa, T. Takamasu, and G. Kido, *J. Phys. Soc. Jpn., Suppl.* **71**, 237 (2002).
- [7] J.-i. Yamaura and Z. Hiroi, *J. Phys. Soc. Jpn.* **80**, 054601 (2011).
- [8] J.-i. Yamaura, S. Yonezawa, Y. Muraoka, and Z. Hiroi, *J. Solid State Chem.* **179**, 336 (2006).
- [9] D. Mandrus, B. C. Sales, and R. Jin, *Phys. Rev. B* **64**, 012302 (2001).
- [10] A. D. Caplin and G. Grüner, *Phys. Rev. Lett.* **30**, 1138 (1973).

- [11] Y. Nagao, J.-I. Yamaura, H. Ogusu, Y. Okamoto, and Z. Hiroi, *J. Phys. Soc. Jpn.* **78**, 064702 (2009).
- [12] T. Dahm and K. Ueda, *Phys. Rev. Lett.* **99**, 187003 (2007).
- [13] K. Hattori, Y. Hirayama, and K. Miyake, *J. Phys. Soc. Jpn.* **74**, 3306 (2005).
- [14] M. M. Koza, M. R. Johnson, R. Viennois, H. Mutka, L. Girard, and D. Ravot, *Nat. Mater.* **7**, 805 (2008).
- [15] E. Bucher, J. P. Maita, G. W. Hull, R. C. Fulton, and A. S. Cooper, *Phys. Rev. B* **11**, 440 (1975).
- [16] M. W. McElfresh, J. H. Hall, R. R. Ryan, J. L. Smith, and Z. Fisk, *Acta Crystallogr., Sect. C* **46**, 1579 (1990).
- [17] K. Takegahara, H. Harima, and T. Kasuya, *J. Phys. F: Met. Phys.* **16**, 1691 (1986).
- [18] B. Renker, F. Gompf, W. Reichardt, H. Rietschel, J. B. Suck, and J. Beuers, *Phys. Rev. B* **32**, 1859 (1985).
- [19] H. Hidaka, Y. Shimuzu, S. Yamazaki, N. Miura, R. Nagata, C. Tabata, S. Mombetsu, T. Yanagisawa, and H. Amitsuka, *J. Phys. Soc. Jpn.* **86**, 043601 (2017).
- [20] H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, *Phys. Rev. Lett.* **50**, 1595 (1983).
- [21] H. M. Mayer, U. Rauchschwalbe, C. D. Bredl, F. Steglich, H. Rietschel, H. Schmidt, H. Wühl, and J. Beuers, *Phys. Rev. B* **33**, 3168 (1986).
- [22] Z. S. Wilson, R. T. Macaluso, E. D. Bauer, J. L. Smith, J. D. Thompson, Z. Fisk, G. G. Stanley, and J. Y. Chan, *J. Am. Chem. Soc.* **126**, 13926 (2004).
- [23] M. Sgrist and K. Ueda, *Rev. Mod. Phys.* **63**, 239 (1991).
- [24] U. Benedict, K. Bujis, C. Dufour, and J. Cl. Toussaint, *J. Less-Common Met.* **42**, 345 (1975).
- [25] J. P. Kappler, G. Krill, M. F. Ravet, G. Heinrich, and A. Meyer, *J. Magn. Magn. Mater.* **15-18**, 965 (1980).
- [26] A. I. Goldman, S. M. Shapiro, D. E. Cox, J. L. Smith, and Z. Fisk, *Phys. Rev. B* **32**, 6042 (1985).
- [27] T. S. Hudson, *J. Phys. Chem. C* **114**, 14013 (2010).
- [28] H. Hidaka, S. Yamazaki, Y. Shimuzu, N. Miura, C. Tabata, T. Yanagisawa, and H. Amitsuka, *J. Phys. Soc. Jpn.* **86**, 074703 (2017).
- [29] S. Mombetsu, T. Murazumi, K. Hiura, S. Yamazaki, Y. Shimizu, H. Hidaka, T. Yanagisawa, H. Amitsuka, S. Yasin, S. Zherlitsyn, and J. Wosnitza, *J. Phys. Conf. Ser.* **683**, 012032 (2016).
- [30] F. Izumi and T. Ikeda, *Solid State Phenom.* **130**, 15 (2007).
- [31] F. Sayetat, P. Fertey, and M. Kessler, *J. Appl. Crystallogr.* **31**, 121 (1998).
- [32] A. Bentien, E. Nishibori, S. Paschen, and B. B. Iversen, *Phys. Rev. B* **71**, 144107 (2005).
- [33] R. D. Shannon, *Acta Crystallogr., A* **32**, 751 (1976).
- [34] Y. W. Yang and P. Coppens, *Acta Crystallogr., A* **34**, 61 (1978).
- [35] S. Tsutsui (private communication).
- [36] C. C. Yu and P. W. Anderson, *Phys. Rev. B* **29**, 6165 (1984).
- [37] H. Kusunose and K. Miyake, *J. Phys. Soc. Jpn.* **65**, 3032 (1996).
- [38] S. Tsutsui, H. Uchiyama, J. P. Sutter, A. Q. R. Baron, M. Mizumaki, N. Kawamura, T. Uruga, H. Sugawara, J.-I. Yamaura, A. Ochiai, T. Hasegawa, N. Ogita, M. Udagawa, and H. Sato, *Phys. Rev. B* **86**, 195115 (2012).