

Crystallography and magnetism of the heavy-fermion compound YbBiPt

R. A. Robinson

*Los Alamos National Laboratory, Los Alamos, New Mexico 87545
and National Laboratory for High-Energy Physics, Tsukuba 305, Japan*

A. Purwanto

*Los Alamos National Laboratory, Los Alamos, New Mexico 87545
and New Mexico State University, Las Cruces, New Mexico 88003*

M. Kohgi

Department of Physics, Tohoku University, Sendai 980, Japan

P. C. Canfield

*Los Alamos National Laboratory, Los Alamos, New Mexico 87545
and Ames Laboratory, Iowa State University, Ames, Iowa 50011*

T. Kamiyama and T. Ishigaki*

Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

J. W. Lynn and R. Erwin

Reactor Radiation Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

E. Peterson and R. Movshovich

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 25 April 1994)

The super-heavy-fermion compound YbBiPt has the largest known linear specific-heat coefficient $\gamma = 8 \text{ J mol}^{-1} \text{ K}^{-2}$, and the source of this enormous "electronic" specific heat is of great current interest. Here we describe neutron-diffraction studies that indicate its previously reported crystallographic structure to be incorrect. We find that the Pt atom is on the unique site and can be thought of as an interstitial in a fictitious rock-salt structure YbBi, which can in turn be thought of as an ordered form of elemental bismuth. We find no evidence of disorder between sites, occupancy on the nominally vacant site, nor for any tetragonal or rhombohedral distortions or displacements. Furthermore, any ordered magnetic moment at low temperature must be less than $0.25\mu_B$. The sample contains 8.1 wt. % elemental Bi, and if this is typical of other samples, the previously published values for molar susceptibilities and specific heats should be scaled up by this amount to obtain the intrinsic properties of YbBiPt alone.

The cubic heavy-fermion compound YbBiPt was discovered in 1991 by Canfield and co-workers^{1,2} and has a very large linear specific-heat coefficient $\gamma = 8 \text{ J mol}^{-1} \text{ K}^{-2}$, an order of magnitude more than that of typical heavy-fermion compounds³ and three orders of magnitude larger than that of conventional metals. YbBiPt forms in the $C1_b$ or MgAgAs structure type (space group $F43m$), which is a common Heusler-alloy structure,⁴ and in which some uranium-based ternaries such as the UNiSn form.⁵ There is only one formula unit per primitive unit cell. It is well known that the conventional face-centered-cubic unit cell is not the primitive cell, and typically the simpler primitive rhombohedral cell⁶ is employed. The atoms are then distributed on three of the four sites along the [111] long diagonal of the rhombohedral cell is listed in Table I. All four sites have tetrahedral point-group symmetry $\bar{4}3m$, but the sequence is not arbitrary in the sense that, if three sites are occupied, one can be thought of as an ordered vacancy, two of the sites have this vacancy as a nearest neighbor, and the

fourth site is *unique*, in that it has no vacant neighbor sites. A previous x-ray study² reported that Bi was on the unique site, and to date two band-structure calculations^{7,8} have assumed this sequence.

In this paper, we describe the results of neutron and x-ray powder-diffraction studies. For these elements the neutron-diffraction contrast is approximately twice that of x rays and opposite in sign. We find that Pt actually occupies the special site rather than Bi. In addition, we address a number of other questions. Firstly, the μSR response⁹ is reminiscent of spin-glass behavior, and it has been suggested that this might be due to nonzero occupancy on the nominally vacant site, or to disorder on the occupied sites. We find no evidence for either. Secondly, there is evidence from inelastic neutron-scattering studies^{10,11} of the crystal-field excitations that the cubic symmetry is broken. We find no evidence for this at room temperature, nor at 0.45 K, even though the "forbidden" crystal-field splitting is seen at temperatures up to 4 K. Finally, bulk measurements and μSR indicate that there

TABLE I. Definition of sites in YbBiPt.

			Order in Ref. 2	Order reported here	Yb on unique site
0,0,0	4a	Unique site	Bi	Pt	Yb
$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	4c		Pt	Bi	BI
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	4b	Vacant site			
$-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}$	4d		Yb	Yb	Pt
Reduced χ^2	Neutrons		1.751	1.554	3.724
	X rays		1.595	1.539	2.592
	Both		1.754	1.554	3.589

is a transition at 400 mK,^{2,9} possibly of antiferromagnetic origin.¹² We have looked for magnetic Bragg peaks in the ordered phase at 50 mK and our data indicate that any ordered moment must be less than $0.25\mu_B$.

The samples were made by growth in a bismuth flux, as reported previously.^{1,13} For the measurements above 4.2 K, a fine powder was used, but for measurements below 4.2 K the material was not ground and consisted of thousands of tiny crystals. The reason for this was that there is evidence that the 400 mK magnetic transition can be suppressed by grinding. Polycrystalline material was sealed under helium gas in a thin-walled aluminum, vanadium, or oxygen-free copper can depending on the sample environment. Full diffraction patterns were measured in closed-cycle helium refrigerators at temperatures between 27 K and room temperature on the HRP powder diffractometer¹⁴ at KENS, the spallation neutron source at the Japanese National Laboratory for High-Energy Physics, and at room temperature on the NPD powder diffractometer¹⁵ at LANSCE, the spallation neutron source at Los Alamos. In addition, further scans were made in a dilution refrigerator at 50 mK and 1.1 K on the BT-9 spectrometer and at temperatures between 0.45 and 10 K in a ³He cryostat on the BT-1 high-resolution powder diffractometer at the Research Reactor of the National Institute of Standards and Technology (NIST). The room-temperature x-ray patterns were recorded on a Scintag XDS2000 powder diffractometer with pyrolytic graphite monochromator and scintillator detector, using $\text{CuK}\alpha$ radiation. The full neutron and x-ray-diffraction scans were analyzed using the Rietveld programs RIETAN (for data taken at KENS) and GSAS for data taken at Los Alamos and NIST. In the refinements reported here, four banks of data (at $\pm 148^\circ$ and $\pm 90^\circ$) from NPD and a single $\text{CuK}\alpha$ X-ray scan were used.

Figure 1(a) shows a portion of the room-temperature data taken on NPD, along with the fitted profile, residuals and markers for YbBiPt and elemental Bi. Figure 1(b) shows similar data taken with x rays. These data were corefined using GSAS (Ref. 15) and the resultant sample parameters are listed in Table II. Figure 2 shows the variation of lattice parameter for YbBiPt between 27 K and room temperature as measured on HRP. The resultant linear coefficient of thermal expansion for YbBiPt is $\alpha = 1.01 \times 10^{-5} \text{ K}^{-1}$ between 70 and 300 K. Many different models were refined. For instance, all three elements were tried on the special site, and Pt is clearly pre-

ferred, as is clear from the reduced values of χ^2 listed in Table I. This is the case if neutron data alone are used, if x-ray data alone are used, or if both are corefined. This conflicts with the previously reported structural positions, and it would clearly be desirable if the electronic band-structure calculations^{7,8} based on this structure could be repeated using the parameters listed in Table II. In fact, placing Pt on the special site makes more sense from atomic size arguments and fits the trend for other MgAgAs compounds,⁵ in which the smaller transition-metal atom invariably occupies the *unique* site, while the

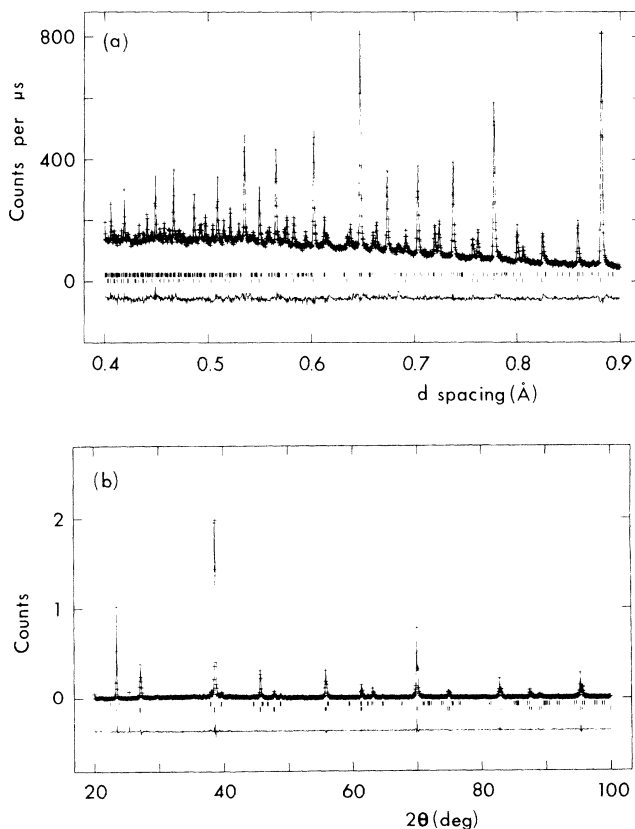


FIG. 1. Portions of room-temperature diffraction data from YbBiPt (with Bi impurity from growth flux), measured (a) with neutrons in NPD Los Alamos and (b) with $\text{CuK}\alpha$ x rays. The refinement is the joint Rietveld refinement described in the text, with parameters given in Table I. The lower reflection markers are for YbBiPt and the upper markers are for elemental Bi.

TABLE II. Crystallographic parameters of YbBiPt at room temperature.

Main phase: YbBiPt	Space group $F\bar{4}3m$	Lattice parameter: $a = 6.59533 \pm 0.000110 \text{ \AA}$		
	Yb	$4d$	$-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}$	$\langle u^2 \rangle = 0.0074 \pm 0.0001 \text{ \AA}^2$
	Pt	$4a$	$0, 0, 0$	$\langle u^2 \rangle = 0.0073 \pm 0.0001 \text{ \AA}^2$
	Bi	$4c$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$\langle u^2 \rangle = 0.0060 \pm 0.0001 \text{ \AA}^2$
	Mosaic block size = $6.1 \pm 0.1 \text{ \mu m}$ (determined from extinction parameter—see Ref. 16)			
Minority phase: elemental Bi ^a	Space group $R\bar{3}m$ (hexagonal axes)	Lattice parameters: $a = 4.5462 \pm 0.0002 \text{ \AA}$ $c = 11.8591 \pm 0.0010 \text{ \AA}$		
	Bi	$6c$	$0, 0, z$	$z = 0.2348 \pm 0.0004$

^a8.3% by volume (8.1% by weight) [7.7% by volume in X-ray sample].

larger f -electron metal and the group-IV/V elements occupy the sites with vacancies as neighbors. If the fractional occupancies are allowed to vary freely in the Rietveld refinement, the resultant stoichiometry is 1:1:1, to within errors of $\pm 2\%$ for the Pt:Yb ratio and $\pm 4\%$ for the Bi:Yb ratio.

It is instructive to note that the crystal structure is closely related to the structure of Bi, the elemental impurity (from the growth flux) in our samples, as shown in Fig. 3. Bismuth is rhombohedral and can be thought of as “distorted” simple cubic. That is, if its c/a ratio were $\sqrt{6} = 2.449$, rather than 2.608 as listed in Table II, and its x position along the trigonal axis ([111] cubic axis) were $\frac{1}{4}$ rather than 0.2348 as listed in Table II, it would be simple cubic. Then, if half the sites were systematically replaced with Yb, it would have the face-centered-cubic sodium-chloride structure shown in Fig. 3(b). Finally, if the small Pt atom is systematically placed in half of the interstitial sites, one has the MgAgAs structure as shown in Fig. 3(c), with the sequence along the [111] axis listed in Tables I and II.

In addition we tried disordering the Yb/Bi sites and placing some of the Pt on the nominally vacant site. The motive for this was that such a site disorder could result in spin-glass behavior in the magnetic degrees of freedom,

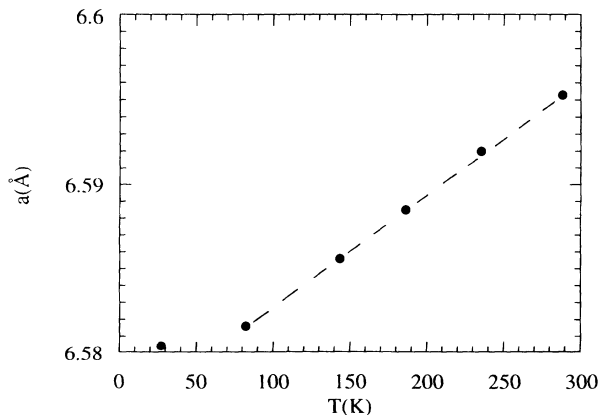


FIG. 2. The variation of lattice parameter with temperature for YbBiPt, as measured by neutron diffraction on HRP at KENS (Ref. 13). The dashed line corresponds to a linear coefficient of thermal expansion of $\alpha = 1.01 \times 10^{-5} \text{ K}^{-1}$.

as has been discussed in the μ SR literature⁹ on YbBiPt. However, we found no evidence in our data of any such disorder. Finally, there is no evidence for any splittings or broadenings of crystallographic lines down to 0.45 K, even though crystal-field data indicate that the cubic symmetry is broken, at least up to 4 K. The lowest-temperature data were taken on many crystals, with so much preferred orientation that reliable Rietveld refinement could not be performed. However, we found no evidence for systematic broadening or splitting in any of the diffraction lines. Rietveld refinements were done on the room-temperature data assuming both tetragonal ($I\bar{4}m2$) and rhombohedral ($R\bar{3}m$) distortions of the parent cubic space group. These are the two maximally

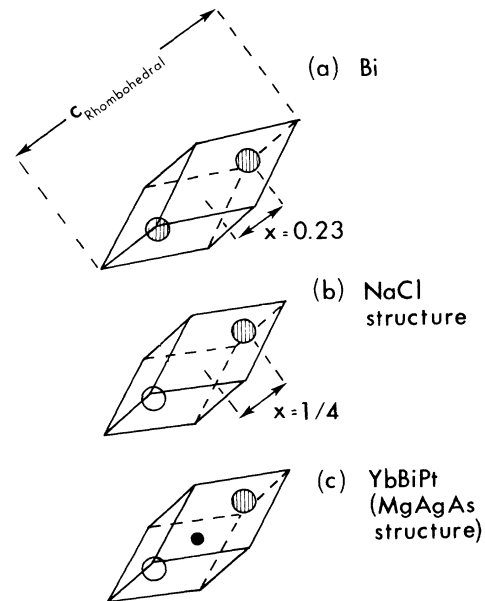


FIG. 3. The relationship between (a) the structure of Bi (rhombohedral with space group $R\bar{3}m$), (b) the fictitious sodium-chloride structure compound YbBi, and (c) the structure of YbBiPt as reported in this paper. Note that (b) is obtained from (a) by compressing the c axis until it reaches the ideal cubic value of $\sqrt{6}a$, replacing every other Bi with Yb and displacing them to $\pm \frac{1}{4}$ (as opposed to ± 0.2348) along the trigonal axis. (c) is obtained from (b) by placing a Pt atom in every other interstitial site. In terms of the coordinates listed in Table I, the origin is in the center of the cell for (a) and (c).

nonisomorphic subgroups of $F\bar{4}3m$, and they correspond to strains along the cubic [111] and [100] axes, respectively. As might be expected, given that no splittings could be observed, there are no significant distortions. Nor were there any significant displacements within the unit cell, for instance the x parameters in $R\bar{3}m$ remained fixed at multiples of $\frac{1}{4}$. To summarize, there is no diffraction evidence for any site disorder, lattice distortions or symmetry-breaking atomic displacements within the unit cell, from the data reported here, at any temperature between 0.45 and 300 K. Of course, there could still be local symmetry-breaking distortions, or the crystal-field splitting could be associated with broken symmetry in the magnetic degrees of freedom.

In order to check the stoichiometry of our samples, wet chemical analysis and x-ray microprobe analysis were also performed, though both turned out to be less sensitive than the Rietveld refinement of diffraction data. Nevertheless, an excess of Bi, consistent with the values given in Table I, was observed in the wet chemical analysis. The presence of the elemental bismuth was also observed by x-ray microprobe analysis. This shows the presence of inclusions a few tenths of a mm in size, within the crystals of YbBiPt. Within experimental error there is no sign of any Yb or Pt dissolved in the Bi phase. The presence of Bi is more important than one might think at first. Many of the thermodynamic properties, like specific heat and magnetic susceptibility, have been reported² as a molar quantities, presumably with sample weights determining the molarities. In particular, the high-temperature magnetic susceptibility has been something of a puzzle: it obeys a Curie-Weiss law with effective moment of $4.2\mu_B$, 92.5% of the full Hund's rule moment for Yb^{3+} . As all the available crystal-field levels have been accounted for by 80 K or so,¹⁷ one would expect to observe the full Hund's rule moment of $4.54\mu_B$.¹⁸ The fact that our sample, which was made by the same

method as others in the literature, contains a nonmagnetic impurity at the 8.1 wt. % level accounts for a large part of this discrepancy. If this is the case for the other samples for which data have been reported, then the intrinsic molar susceptibilities and specific heats of YbBiPt are almost 10% larger than those reported in the literature.

The other question that can be addressed by means of neutron diffraction regards the nature of the ground state, below the 400-mK phase transition.² The exact nature of this transition is as yet unknown, but there is good evidence that it is magnetic.¹² We therefore conducted a search for magnetic Bragg peaks at 50 mK, using the BT-9 spectrometer at NIST. Data were also taken at 1.1 K, and these were subtracted from the 50-mK data. No extra magnetic signal was observed between $Q=0.28$ and 2.83 \AA^{-1} . Error analysis of the hypothetical 100 magnetic reflection, with the known spectrometer resolution indicates that the limit of observability in our experiment is $0.25\mu_B$. This is not inconsistent with the estimate from μSR measurements, indicating that the ordered moment is $0.1\mu_B$ or less.

ACKNOWLEDGMENTS

We are grateful to T. Foreman for doing the chemical analysis, J. F. Smith for help with the microprobe and R. B. Von Dreele for advice concerning the Rietveld refinement. We are also glad to acknowledge a number of helpful discussions with G. Aeppli and W. P. Beyermann. One of us (R.A.R.) is very grateful to the Japanese Ministry of Science and Education, MONBUSHO, for financial support and to the staff of the National Laboratory for High-Energy Physics for their hospitality while in Japan. This work was funded in part by the division of Basic Energy Sciences of the U.S. Department of Energy.

*Present address: Muroran Institute of Technology, Mizumotocho, Muroran, Hokkaido 050, Japan.

¹P. C. Canfield, J. Thompson, W. P. Beyermann, A. Lacerda, M. F. Hundley, E. Peterson, Z. Fisk, and H. R. Ott, *J. Appl. Phys.* **70**, 5800 (1991).

²Z. Fisk, P. C. Canfield, W. P. Beyermann, J. D. Thompson, M. F. Hundley, H. R. Ott, E. Felder, M. B. Maple, M. A. Lopez de la Torre, P. Visani, and C. Seaman, *Phys. Rev. Lett.* **67**, 3310 (1991).

³Z. Fisk, D. W. Hess, C. J. Pethick, D. Pines, J. L. Smith, J. D. Thompson, and J. O. Willis, *Science* **239**, 33 (1988).

⁴See, for instance, Y. Ishikawa and Y. Noda, in *Magnetism and Magnetic Materials*, Proceedings of the 20th Annual Conference on Magnetism and Magnetic Materials, San Francisco, 1974, edited by C. D. Graham, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1975), p. 145.

⁵M. Yethiraj, R. A. Robinson, J. J. Rhyne, J. A. Gotaas, and K. H. J. Buschow, *J. Magn. Magn. Mater.* **79**, 355 (1989).

⁶See, for instance, C. Kittel, *Introduction to Solid-State Physics*, 5th ed. (Wiley, New York, 1976), p. 17.

⁷O. Eriksson, J. M. Wills, and A. M. Boring, *J. Alloys Compounds* **185**, 145 (1992).

⁸G. J. McMullan and M. P. Ray, *J. Phys. Condens. Matter* **4**,

7095 (1992).

⁹A. Amato, P. C. Canfield, R. Feyerherm, Z. Fisk, F. N. Gygax, R. H. Heffner, D. E. McLaughlin, H. R. Ott, A. Schenck, and J. D. Thompson, *Phys. Rev. B* **46**, 3151 (1992).

¹⁰R. A. Robinson, M. Kohgi, T. Osakabe, F. Trouw, J. W. Lynn, P. C. Canfield, T. Kamiyama, T. Nakane, J. D. Thompson, and Z. Fisk (unpublished).

¹¹C. Broholm, T. Mason, G. Aeppli, R. A. Robinson, and P. C. Canfield (unpublished).

¹²R. Movshovich, A. Lacerda, P. C. Canfield, J. D. Thompson, and Z. Fisk, *Phys. Rev. Lett.* **73**, 492 (1994).

¹³P. C. Canfield and Z. Fisk, *Philos. Mag. B* **65**, 1117 (1992).

¹⁴N. Watanabe, H. Asano, H. Iwasa, S. Satoh, H. Murata, K. Karahashi, S. Tomiyoshi, F. Izumi, and K. Inoue, *Jpn. J. Appl. Phys.* **26**, 1164 (1987).

¹⁵A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LA-UR-86-748, 1986 (unpublished).

¹⁶T. M. Sabine, R. B. Von Dreele, and J.-E. Jorgensen, *Acta Cryst. A* **44**, 374 (1988).

¹⁷R. A. Robinson, M. Kohgi, T. Osakabe, P. C. Canfield, T. Kamiyama, T. Nakane, Z. Fisk, and J. D. Thompson, *Phys. B* **186-188**, 550 (1993).

¹⁸See, for instance, C. Kittel, *Introduction to Solid-State Physics*, 6th ed. (Wiley, New York, 1976), p. 405.