On the Magnetic Interactions in Metal-Be$_{13}$ Compounds

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(Received 3 June 1996)

We report magnetization, Mössbauer, and neutron experiments to determine the low-temperature magnetic structure of the heavy-fermion compound NpBe$_{13}$. The magnetic wave vector is $\mathbf{q} = \langle \frac{1}{3}\ 0\ 0 \rangle$, and nearest neighbor moments are oriented perpendicular to each other. We have found an unusual modulation of the moments, which reflects the influence of the strong Kondo interaction. Comparisons are made with the magnetic arrangements found in the rare-earth Be$_{13}$ compounds, and it is concluded that a search for magnetic correlations in UBe$_{13}$ should be concentrated around this wave vector. [S0031-9007(96)01499-8]

PACS numbers: 75.25.+z, 75.30.Mb, 78.80.+y,

Uranium based heavy-fermion (HF) superconductors (UPt$_3$, UBe$_{13}$, URu$_2$Si$_2$, UPd$_2$Al$_3$, and UNi$_2$Al$_3$) have attracted wide interest because of the interplay between magnetism and superconductivity, and the suspicion that the superconductivity is of the so-called *d* type, rather than the usual *s* type [1]. So far, all of the uranium-based HF superconductors, with one exception, are found to order antiferromagnetically with $T_N > T_c$. In some cases, URu$_2$Si$_2$ [2] and UPt$_3$ [3], there is evidence that the order is not truly long range, but the magnetic correlations are certainly strong. The exception is UBe$_{13}$, a cubic material with $T_c = 0.85$ K and a linear coefficient of the specific heat $\gamma = C/T = 1100$ mJ/(mole K^2) [4], and in which no magnetic correlations have been reported despite experiments with muons [5] and neutrons [6]. Nothing is known therefore about $\chi(\mathbf{q})$, the wave-vector-dependent magnetic susceptibility, in UBe$_{13}$. The absence of evidence for magnetic correlations in this one compound prevents generalizations that might lead to theoretical advances.

In this Letter we report experiments on NpBe$_{13}$, the isostructural homolog of UBe$_{13}$. The addition of one extra 5*f* electron in substituting Np for U reduces the lattice parameter by a mere 0.16% [from $a_0 = 10.249$ Å at 10 K in UBe$_{13}$ [7] to 10.233(4) Å at 10 K in NpBe$_{13}$]. We therefore expect NpBe$_{13}$ and UBe$_{13}$ to have the same metal ion valency, and to have a similar conduction-electron density (arising principally from the Be *s* electrons), but to vary in their *f*-electron ground-state configurations, $5f^n$ for UBe$_{13}$ and $5f^{n+1}$ for NpBe$_{13}$.

Shortly after the discovery of superconductivity in UBe$_{13}$, Stewart *et al.* [8] investigated NpBe$_{13}$ and found that (1) the compound orders antiferromagnetically at 3.4 K, (2) there is a large temperature-dependent specific heat above T_N which corresponds to $\gamma \approx 900$ mJ/(mole K^2) so that, like its analog UBe$_{13}$, NpBe$_{13}$ is a heavy-fermion compound, and (3) NpBe$_{13}$ is not superconducting down to 0.080 K. Subsequent work on NpBe$_{13}$ using the Mössbauer technique [9] showed that the low-temperature properties were sensitive to Be content. Samples with excess Be were nonmagnetic. The samples exhibiting the clearest magnetic properties had $T_N = 4.9$ K and a hyperfine field corresponding to an ordered moment of $\approx 1\mu_{\mathrm{B}}$ per Np atom.

The goal in our experiments was to characterize the magnetic structure of NpBe$_{13}$ with Mössbauer, magnetic susceptibility, and neutron experiments in an attempt to understand further the magnetic interactions of the actinide-Be$_{13}$ compounds.

The sample was prepared at Los Alamos National Laboratory by arc melting high-purity elements. To homogenize the sample a batch of ≈5 g was annealed for 1 week at $T = 1500\,^{\circ}$C. A test at low temperature with the Mössbauer technique (at Karlsruhe) showed that the annealed sample was completely magnetic. The Mössbauer spectrum is shown in Fig. 1. The temperature dependence of the spectra shows that T_N is about 5 K. At low temperature the spectra can be accounted for only by assuming that there are two hyperfine fields with values corresponding [10] to magnetic moments $\mu_a = 1.12(5)\mu_{\mathrm{B}}$ and $\mu_b = 0.97(5)\mu_{\mathrm{B}}$. The intensity ratio corresponds to twice [1.9 ± 0.2] as many moments with μ_a as with μ_b. Since the MBe$_{13}$ structure has only one equivalent M site (see below), this analysis of the Mössbauer spectra indicates that a modulated magnetic structure exists. The isomer shift is 3.1(2) mm/sec (as found in Ref. [9]) with respect to NpAl$_2$, and this suggests that the Np ion is trivalent [10]. The absence of any appreciable induced quadrupolar interactions in the Mössbauer spectra is consistent with a Γ_5 ground state.

Magnetic susceptibility and magnetization measurements were obtained on an annealed polycrystalline sample of 24 mg at the SHE-SQUID magnetometer of the CEA-Grenoble with applied fields up to $B = 5$ T, and in the temperature range $2\ \mathrm{K} < T < 300$ K. The χ and $1/\chi$ curves as a function of T are shown in Fig. 2. The maximum (inset) appears at $T_N = 4.6$ K, and is reduced to

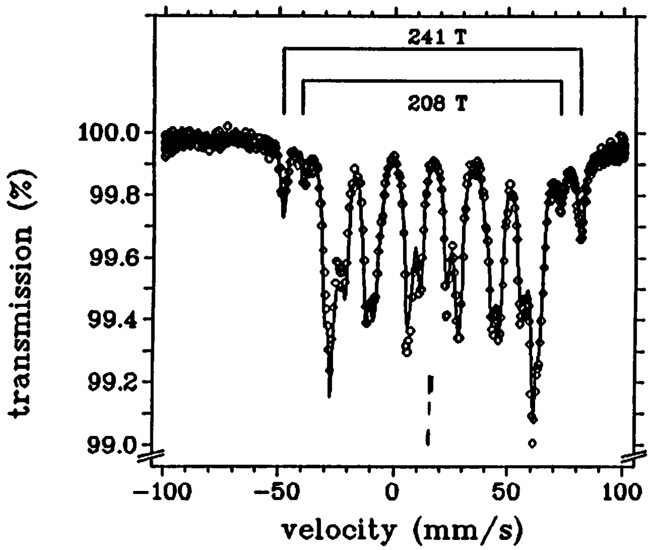

FIG. 1. Mössbauer absorption spectrum of annealed $NpBe_{13}$ at 1.3 K. For the nonmagnetic samples a single line is observed at the position of the dashed vertical line. The solid line is the result of least-squares fitting two Np Mössbauer patterns to the observed spectrum. The corresponding hyperfine fields are shown by the bars at the top and are 241(2) T and 208(3) T.

4.1 K with $B = 5$ T. From the high-temperature region we find $\mu_{\mathrm{eff}} = 2.2(1)\mu_{\mathrm{B}}$, which is consistent with that expected ($2.15\mu_{\mathrm{B}}$) from a Np^{3+}:$5f^4$ configuration with a Γ_5 (magnetic) triplet as the ground state.

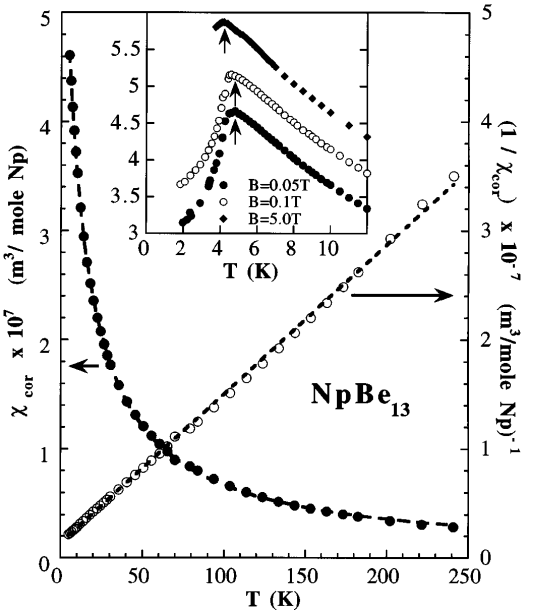

FIG. 2. Susceptibility and $(1/\chi)$ for the $NpBe_{13}$ powder sample as a function of temperature. The data were corrected for the Al sample container and for a small amount of ferromagnetic impurity (possibly NpC) assuming that the latter is saturated at high fields. The dashed line through the $(1/\chi)$ points signifies $\mu_{\mathrm{eff}} = 2.2\mu_{\mathrm{B}}$ per Np atom. The inset shows the variation of χ around T_N and the dependence of the latter on applied field. The curves for $B = 0.1$ and 5.0 T have been offset by 0.5 and 1.0 units, respectively.

Neutron-diffraction experiments were performed on a polycrystalline sample of 3.9 g and a small single crystal of ≈ 1 mg at the Siloë reactor (CEA-Grenoble) using the instrument DN5 ($\lambda = 2.49$ Å) with a multidetector for the polycrystalline sample, and the instrument DN3 ($\lambda = 1.52$ Å) with a lifting-arm detector for the single crystal. The room-temperature diffraction patterns confirmed the cubic fcc structure of the $M\mathrm{Be}_{13}$ compounds. We show this structure in Fig. 3(a). There are 8 M atoms in the unit cell, divided into two sets of 4 that are connected by the body-centering operator $+(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$. Within each set of 4 the positions are related by the face-centering operator $+(\frac{1}{2}\,\frac{1}{2}\,0)$, and the initial atom position is $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$. Figure 3(b) shows the results of subtracting the data taken at $T = 10$ K from identical low-temperature scans

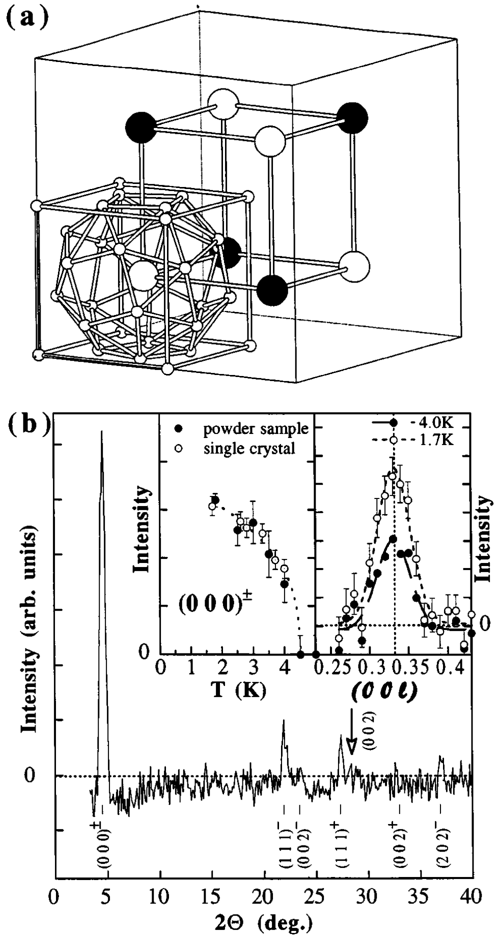

FIG. 3. (a) Crystallographic structure of the $M\mathrm{Be}_{13}$ compounds. The two different Bravais lattices of the M atoms are shown as open and black spheres. Each M atom is surrounded by a polyhedron of 24 Be atoms (small open spheres) at a distance of ≈ 3.0 Å. The nearest M-M distance is $a_0/2 = 5.12$ Å. (b) The main figure shows the low-angle part of the difference pattern $I(T = 1.5\ \mathrm{K}) - I(T = 10\ \mathrm{K})$ obtained from the polycrystalline sample. The magnetic reflections are indexed and the position of the nuclear (0 0 2) peak marked. The insets show (left) the intensity of the $(0\ 0\ 0)^{\pm}$ satellite as a function of temperature and (right) the intensities from the single crystal as a function of wave vector at two different temperatures.

($T < T_N$). The main figure shows a strong peak at $(0\ 0\ 0)^{\pm}$, and four other weaker peaks. The additional magnetic reflections may be indexed as $(H\ K\ L)^{\pm q}$, where $q = 0.33(2)$ reciprocal lattice units (rlu). The wave vector of the modulation may be written $\mathbf{q} = \langle \frac{1}{3}\ 0\ 0 \rangle$, where the cubic symmetry ensures that $\mathbf{q}$ may be along any one of the cube axes, and is independent of temperature. The magnetic unit cell is thus 3 times as large as the chemical unit cell along the propagation direction and consists of 6 layers, each containing 4 Np moments.

Despite the small size of the single crystal (≈ 0.5 mm^3), important new information (as well as confirmation of the powder experiment) was obtained in the experiment on DN3. The temperature dependence of the $(0\ 0\ 0)^{\pm}$ satellite from both experiments is shown in the inset of Fig. 3(b). They are both consistent with $T_N = 4.5(2)$ K. An important confirmation was the presence of magnetic peaks around the ($H\ K\ L$ all odd) nuclear reflections such as (1 1 1), which are not allowed in the nuclear structure pattern because of the body-centering operator. A further aspect of the experiments was to search for the presence of higher-order satellites of the form $(H\ K\ L)^{\pm pq}$, where $p > 1$. For a squared magnetic modulation with this $\mathbf{q}$ vector we anticipate such a component with an amplitude ratio between the third- and first-order components of 0.25. Our experimental results imply that this ratio A_{3q}/A_q is less than 0.20.

To determine the details of the magnetic structure we note first that the presence of a strong $(0\ 0\ 0)^{\pm}$ satellite proves the magnetic moments are perpendicular to the wave vector $\mathbf{q}$. This is because group theory allows the moments to be either parallel or perpendicular to $\mathbf{q}$ (and not at any intermediate angle), and scattering at $(0\ 0\ 0)^{\pm}$ is proof that it is perpendicular. Recall that neutrons are sensitive to the components of the magnetization perpendicular to the scattering vector (or momentum transfer) $\mathbf{Q}$. A second important observation is the presence of magnetic satellites around the forbidden ($H\ K\ L$ all odd) nuclear reflections. By writing

$$\mathbf{m}_1 = (m_x, m_y, 0), \qquad \mathbf{m}_2 = (m_x, -m_y, 0)$$

and with $\mathbf{q} = (0, 0, \frac{1}{3})$, where $\mathbf{m}_j$ represent magnetization vectors on the two separate Bravais lattices, we model the system with all moments lying in the (xy) plane and the propagation direction parallel to z. A pure ferromagnetic in-plane coupling may be simulated by $m_y = 0$, which will give rise to magnetic satellites around only the ($H\ K\ L$ all even) nuclear reflections, whereas a pure antiferromagnetic coupling may be written as $m_x = 0$, and will give magnetic satellites around only the ($H\ K\ L$ all odd) nuclear reflections. If both are present then the angle α between the moments on nearest neighbor M atoms [see Fig. 3(a)] will be given by $\alpha = 2\arctan(m_y/m_x)$. Refining the observed intensities we find $m_x = 0.52(1)\mu_{\mathrm{B}}$ and $m_y = 0.55(3)\mu_{\mathrm{B}}$, so that within our precision, α is $\pi/2$. We define the amplitude of the first harmonic $A_q = |m_1| = |m_2|$. The neutron experiments cannot tell where in the (xy) plane the moments lie. The data are consistent with any choice of two orthogonal axes.

For one Bravais lattice the moments $\mu(i)$ in the ith layer perpendicular to $\mathbf{q} = (0, 0, \frac{1}{3})$ are given by

$$\mu(i) = 2\sum_p A_{pq}\sin\left(2\pi pq\,\frac{i-1}{2} + \phi_{pq}\right),$$

where ϕ_{pq} is an arbitrary phase angle. Diffraction measurements of the type performed here are insensitive to the phase angles. The second Bravais lattice may be similarly described, although with an additional arbitrary phase factor. The problem is simplified because for this $\mathbf{q}$ vector only two harmonics with $p = 1$ and 3 exist. The requirement for the third order ($p = 3$) is necessary as a single order ($p = 1$), representing a sinusoidal modulation of the magnetic moments, cannot explain the population of moments as found in the Mössbauer experiments, irrespective of the choice of ϕ. In fact, by choosing $A_{3q} = 0.2A_q$ (which is just at the limits of our detection), $\phi_q = 35°$ and $\phi_{3q} = 90°$ we arrive at the structure illustrated in Fig. 4. The magnetic moments are then $\mu_a = 1.16(3)\mu_{\mathrm{B}}$ and $\mu_b = 0.94(3)\mu_{\mathrm{B}}$, and the choice of phase angles assures that there are twice as many μ_a as μ_b, entirely consistent with the Mössbauer spectrum at low temperature.

The unusual magnetic structure found in NpBe$_{13}$ may be compared to that found in MBe$_{13}$ (where M = Gd,

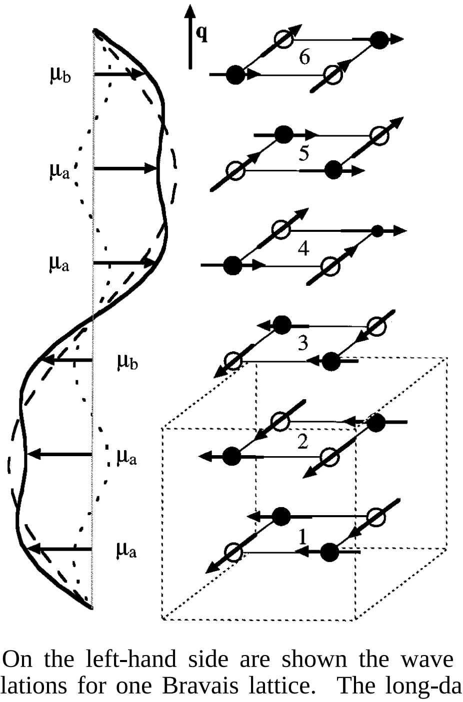

FIG. 4. On the left-hand side are shown the wave forms of the modulations for one Bravais lattice. The long-dashed line is the ($p = 1$) first harmonic and the short-dashed the ($p = 3$) third harmonic. They combine together to give the modulation shown by the solid line, which is the envelope describing the magnitudes of the magnetic moments. On the right-hand side are shown three chemical unit cells (the first outlined). The moments are perpendicular to the propagation direction, and the two sublattices [see Fig. 3(a)] have their moments perpendicular to each other.

Tb, Dy, Ho, and Er) [11]. In most of these materials at low temperature $\mathbf{q} = \langle \frac{1}{3}\ 0\ 0 \rangle$, Gd being an exception with $q = 0.284$ rlu. In all these rare-earth compounds the form of the modulation consists of a simple or bunched helix, and the intraplanar coupling is ferromagnetic. There are no satellites around the (1 1 1) reflection. Becker *et al.* [12] have explained these structures in terms of a model involving exchange integrals between localized $4f$ moments and competition with the magnetocrystalline anisotropy. Despite the major difference between the magnetic arrangements found in $\mathrm{NpBe_{13}}$ and the rare-earth $\mathrm{Be_{13}}$ compounds, there is a remarkable common feature—the wave vector of the modulation. We argue that the metal ions in all these compounds are trivalent and this wave vector is a consequence of the $\mathbf{q}$-dependent susceptibility $\chi(\mathbf{q})$ of the conduction electrons. The direct M-M exchange must be small as the M-M distance ($= a_0/2$) exceeds 5 Å. If Np in this material is trivalent ($5f^4$ configuration), which is suggested by the isomer shift, then we would expect U to be also trivalent in $\mathrm{UBe_{13}}$ ($5f^3$ configuration) and evidence for magnetic correlations might well appear at the same wave vector, i.e., $\mathbf{q} = \frac{1}{3}$.

The importance of the Kondo effect may be seen in the stabilization of the modulation in $\mathrm{NpBe_{13}}$. Normally, at low temperatures, entropy considerations demand a squaring of the magnetic modulations so that all moments are equal in magnitude. For the Γ_5 ground state of $\mathrm{Np^{3+}}$ the full moment would be $1.54\mu_{\mathrm{B}}$, so that the Kondo effect produces a compensating modulation in the conduction-electron gas. Such a modulation is found also in $\mathrm{NpRu_2Si_2}$ [13].

The novel “perpendicular arrangement” of moments in $\mathrm{NpBe_{13}}$ has the property that all six nearest neighbors have their moments perpendicular to that of the central atom. Thus the normal exchange interaction term $\mathbf{J} \cdot \mathbf{J}$ is identically zero, and the structure must be stabilized by higher-order terms, and/or strong coupling to the lattice [14].

In conclusion, the magnetic structure of the heavy-fermion compound $\mathrm{NpBe_{13}}$ has been determined with a combination of neutron and Mössbauer experiments. The resulting perpendicular arrangement is quite different from that found in the isostructural $4f$ compounds, but the wave vector is identical. The strong Kondo effect due to hybridization of the $5f$ and conduction electrons is observed in the ordered state, and the wave vector of the structure gives new information on where to search for magnetic correlations in $\mathrm{UBe_{13}}$.

It is a pleasure to acknowledge Gabriel Aeppli for the original idea to perform these experiments, and Greg Stewart for comments on the manuscript. Support given to A. H., J. C. W., and S. Z. in the frame of the EC funded training program (Human Capability and Mobility) is acknowledged. We thank members of the technical staff at Los Alamos, EITU, Karlsruhe, and the CEA-Grenoble for assistance with transporting and handling these radioactive samples.

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