NMR determination of the B substitutional site in $UBe_{13-x}B_x$

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We report ^{9}Be, ^{10}B, and ^{11}B NMR measurements in $U(Be,B)_{13}$ which show an exclusive substitution site for the boron dopant into the $m3$ or cubic site of the UBe_{13} lattice.

I. INTRODUCTION

Recently, there has been much interest in the effect of doping small amounts of boron into the unconventional heavy-fermion superconductor UBe_{13}. $UBe_{13-x}B_x$ ($x \sim 0.03$) has been shown to exhibit several remarkable properties.[1-4] The most striking is the large enhancement in the specific-heat discontinuity ΔC at the superconducting transition temperature (T_c). ΔC shows a strong boron concentration dependence which reaches a maximum value for $x \sim 0.03$, nearly twice as large as in the pure compound. The effect of B doping on T_c is small,[4] which is in sharp contrast to what is observed when other nonmagnetic impurities are substituted for Be at comparable doping levels.[5] Also, there is evidence[3,4] for a systematic reduction in the energy scale associated with spin fluctuations as the B concentration is increased. It has been suggested that these observations provide evidence for a correlation between the superconducting coupling strength and the energy scale characterizing these spin fluctuations.[3,4]

The compound UBe_{13} crystallizes in the cubic $NaZn_{13}$ structure[6] with eight formula units per unit cell. The space group is O_h^6-$Fm3c$, with eight equivalent U in $\pm(1/4,1/4,1/4)$, and two nonequivalent Be sites: eight Be(I) in $\pm(0,0,0)$, $\pm(1/2,1/2,1/2)$ and 96 Be(II) at $\pm(0,y,z)$, $\pm(0,y,\bar{z})$, $\pm(1/2,z,y)$, $\pm(1/2,\bar{z},y)$, plus threefold rotation and face centering equivalent positions. The values of y and z have been calculated to be 0.1761 and 0.1141, respectively. Of importance to our discussion is that Be(II) possesses cubic symmetry ($m3$), whereas the symmetry of Be(II) is lower (m). The Be(I) is located at the center of an icosahedron formed by 12 nearest-neighbor Be(II) sites. This configuration is, surprisingly, isostructural to the nearest-neighbor configuration of hcp Be metal. The sublattice consisting of only U and Be(I) atoms forms a simple CsCl-type structure. Shown in Fig. 1 is a formula unit cell displaying both nonequivalent Be sites. The U site (not shown) is approximately located at the cube's center. The faces of the cube show the 24 nearest-neighbor Be(II) sites to U, which are located on the corners of a 38-sided polyhedron or snub cube.

Because of the similarity of ionic radii of Be^{2+} and B^{3+}, one expects that B will be substituted into a Be site. There are, however, other possibilities for the B substitution. The phase diagrams for the U-B and B-Be systems show that it may be possible to precipitate a second phase instead of forming the compound $UBe_{13-x}B_x$. For example, unlike the U-Be system where UBe_{13} is the only stable compound, the U-B system can stabilize three compounds UB_2, UB_4, and UB_{12}. Any of these compounds could be a potential second phase. Other possibilities for the B location include an interstitial lattice position other than a specific crystallographic site, or the deposition of elemental B in grain boundaries. Indirect evidence that the B is actually entering into the material and affecting the electronic properties can be seen in heat-capacity and resistivity measurements.[1-4] X-ray-diffraction experiments observe no detectable changes in lattice parameters despite the slightly smaller ionic radius of B. However, x-ray-scattering diffraction is limited in sensitivity because the amount of substituted B is extremely small and because of the difficulty in detecting the presence of light elements with a small x-ray-scattering cross section such as B.

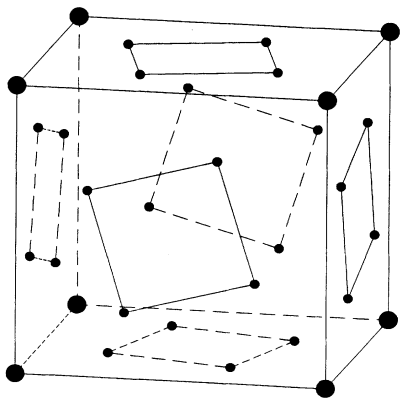

FIG. 1. One formula unit cell of UBe_{13} showing both nonequivalent Be sites and the B doping site. The U site is not shown and is located at approximately the cube's center.

A local probe such as NMR provides a powerful tool for elucidating impurity structures. Within a given sample of $UBe_{13-x}B_x$ we are able to detect NMR resonances from three nuclei: ^{9}Be, ^{11}B, and ^{10}B. A simple analysis of the field-swept spectra for the three nuclei is presented which exploits the known quadrupolar interaction parameters established from detailed single-crystal studies [7] of pure UBe_{13}. The results indicate that the B is substituted exclusively into the cubic Be_1 site. Measurements of the spin-lattice-relaxation rate $(1/T_1)$ of the B nuclei indicate that all the substituted B resides in a single phase of the sample and exhibits the characteristic enhancement of the density of sates at the Fermi energy seen in pure UBe_{13} and many other heavy-fermion compounds.[8]

II. EXPERIMENT

A number of compositions of polycrystalline $UBe_{13-x}B_x$ were prepared using a standard arc-melting technique. The B concentrations studied were $x=0.010$, 0.030, and 0.067 from the same series of samples used in thermodynamic, transport, and μSR studies.[2–4] The NMR samples were prepared from portions of polycrystalline ingots which were powdered to particle sizes of diameter $38 \leq d \leq 125$ μm. Ten percent by volume of -325 mesh, 99.99% Al was mixed in with the sample as a local-field reference for shift measurements. Approximately one gram of sample was used per B concentration. NMR spectra were obtained with a conventional pulsed NMR spectrometer by integrating the spin-echo intensity with a boxcar integrator while sweeping the applied magnetic field. The spin-lattice-relaxation rate was measured by integrating the spin-echo intensity at various times after a comb of saturating pulses. The time dependence of the recovery of the magnetization fit a single exponential.

In order to confirm that the boron concentration is approximately equal to the nominal values, we measured the relative number of ^{11}B to ^{9}Be nuclei in each sample using NMR. This was obtained from the ratio of the integrated areas under the field-swept spectra for ^{11}B and ^{9}Be within a given sample. These measurements were made at constant frequency and corrections were made for the relative sensitivity and T_2 for the respective nuclei. The values obtained are in agreement with the nominal values to better than 35%. But more importantly, this measurement confirms that the B resonance we observe includes essentially all the boron in the sample.

III. RESULTS AND DISCUSSION

Field-swept spectra for the ^{9}Be, ^{11}B, ^{10}B, and ^{27}Al nuclei in the $x=0.030$ sample are shown in Fig. 2. The field axis for each spectrum taken at various spectrometer frequencies is normalized to the centroid of each resonance, except for the ^{9}Be spectrum which is normalized to the approximate position of the Be(I) feature. In Fig. 3 we plot the field dependence of the linewidths of the ^{11}B, ^{10}B, and ^{27}Al nuclei, obtained from the full width at half maximum (FWHM) for a Gaussian fit.

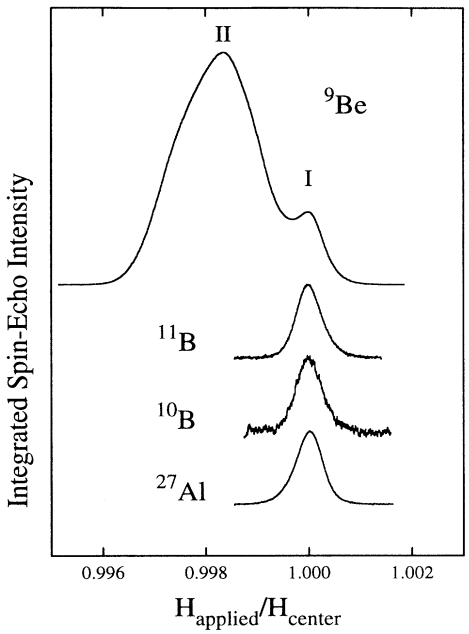

FIG. 2. Field-swept spectra taken at 4 K for the ^{9}Be, ^{11}B, ^{10}B, and ^{27}Al in the $x=0.030$ sample. The field axes are normalized to the center of reach resonance, except for the ^{9}Be spectrum which is normalized to the approximate position of the Be(I) feature (labeled). Note the absence of a Be(II) feature in the B resonances and the comparable widths and line shapes of ^{11}B, ^{10}B, and ^{27}Al. The spectra taken at spectrometer frequencies of 52 MHz for ^{9}Be and ^{10}B, and 95 and 63 MHz for ^{11}B and ^{27}Al, respectively.

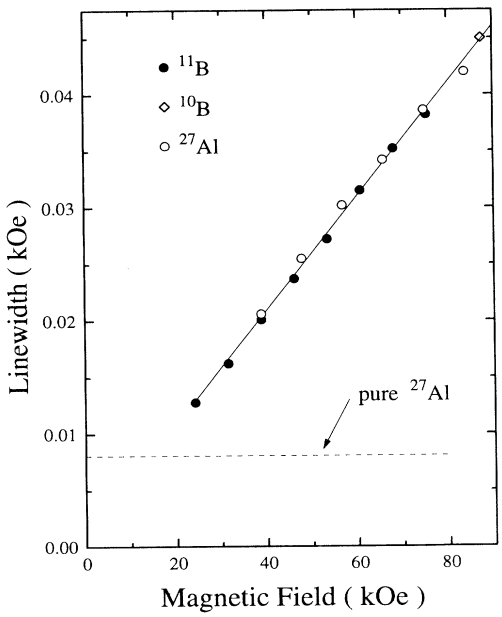

FIG. 3. Magnetic-field dependence of the linewidth for ^{11}B, ^{10}B, and ^{27}Al, measured from the FWHM for a Gaussian fit. All linewidths follow the same linear field dependence resulting from the large χ_V of the powdered sample. The approximately field-independent linewidth of pure Al is also shown for comparison.

The ^{9}Be spectrum shows two features comprising both nonequivalent Be sites. The low symmetry of the Be(II) site gives rise to a quadrupolar interaction of strength,[7]

$$\nu_Q = 3e^2Qq/2I(I-1)h = 328 \text{ kHz} , \quad (1)$$

where eq is the strength of the electric-field gradient (EFG), Q is the value of the quadrupole moment, and $I=3/2$ is the nuclear spin for ^{9}Be. This is convoluted with a small anisotropic Knight shift and magnetic broadening, forming a broad powder pattern. The cubic symmetry of the Be(I) site means that both the EFG and the anisotropic Knight shift are zero. This site contributes one-thirteenth of the total spectral weight and exhibits a symmetric line shape which partially overlaps the Be(II) line. The ^{11}B and ^{10}B nuclei have spin $I=3/2$ and $I=3$ and a natural abundance of 80.2 and 19.8 %, respectively. The spectra of both nuclei exhibit a single, approximately Gaussian line shape. In order to analyze the B spectra, we start by considering the expected quadrupolar split powder pattern for B randomly substituted into both Be sites. We will assume that the EFG at a boron impurity in a Be(II) site is equal to the value measured in pure UBe_{13}. In general, however, one expects a modification to the electronic contribution to the EFG as a result of the substitution of trivalent B^{3+} for divalent Be^{2+}. This orginates from at least two sources. First, there is an additional local electronic contribution to the EFG due to the necessity for additional conduction-electron screening of the excess charge, which generally results in a small enhancement of the strength of the EFG [9]. Second, there is a difference in the Sternheimer antishielding factor between Be^{3+} and B^{2+}. This is a small effect, however, because the two ions have identical core electron configurations. One can estimate the hypothetical "width" of a Be(II) feature in a ^{11}B spectrum from the magnitude of $\nu_Q(^{11}\text{B})$. This is a measure of the splitting between quadrupolar satellites and approximates the width of the resulting quadrupolar powder pattern. The value of the quadrupole moment Q of ^{11}B is 80% of that of Be, which gives $\nu_Q(^{11}\text{B}) \sim 262$ kHz. This yields a line of width ~ 192 Oe, several times the observed ^{11}B linewidth within the measured field range (Fig. 3). For a random substitution of B into both Be sites, the ^{11}B spectrum would have the same two features as the Be spectrum, except for a slightly smaller overall width at a constant field. The ^{10}B has $I=3$ and a value of Q that is 60% greater than Be. Expression (1) gives $\nu_Q(^{10}\text{B}) \sim 131$ kHz and a splitting between only the inner pair of the six satellites of ~ 287 Oe, again much greater than the observed linewidth (Fig. 3). The observation of a single line for both B spectra and the absence of quadrupolar broadening is explained if the boron is located at a point of cubic symmetry where the EFG is zero.

Next we consider the effect of an interstitial B substitution. This would create local disorder around the impurity site and thus a distribution in the local EFG. First-order quadrupolar interactions due to this distribution would have a different effect on the linewidths of half-integral and integral spin nuclei. For half-integral spin nuclei such as ^{11}B, the effect is to broaden or make the satellites completely unobservable, but leave the width of the central transition ($m=\frac{1}{2}\leftrightarrow-\frac{1}{2}$) unaffected. In integral spin nuclei like ^{10}B, the same EFG distribution would cause a broadening of all allowed transitions, making the overall linewidth broader than that of ^{11}B. The observation of comparable linewidths for constant applied magnetic field for both ^{11}B and ^{10}B cannot be explained if a significant distribution in EFGs existed at the B substitution site, and thus an interstitial B substitution is unlikely.

The field dependence of the linewidth for the ^{11}B nuclei was investigated in order to determine the origin of the width and to look for evidence of an anisotropic Knight shift. Figure 3 shows the ^{11}B results for the $x=0.030$ sample at $T=4$ K. We also observe that the widths of the ^{10}B and ^{27}Al lines have identical field dependences and therefore the same broadening mechanism is dominant for all three nuclei. One expects bulk sample magnetic-field inhomogeneities to have an important contribution to the line shape because of the huge susceptibility of these materials.[10] Drain discusses two magnetic line broadening mechanisms for a paramagnetic sample of packed spheroids.[11] The first is due to the dipole fields from the surface magnetization of neighboring particle grains. This causes a symmetric broadening of roughly Gaussian line shape. The second interaction causes an asymmetric broadening due to variations in internal demagnetization fields within individual particles as a result of deviations from sphericity. Broadening due to the first mechanism has been estimated[11] assuming a cubic close-packed ensemble of spherical particles to be $\Delta H \cong 3\chi_V H_0$ at the FWHM, where χ_V is the volume susceptibility and H_0 is the applied field. The slope of a least-squares fit through the linewidth data in Fig. 3 is 5.01×10^{-4} and is in good agreement with $3\chi_V$, where the measured bulk susceptibility is $\chi_V = 1.64\times10^{-4}$ emu/cm^3 at 4 K. Thus, the Gaussian line shape and magnitude of the linewidth for the three nuclei can be explained by classical magnetic effects. These observations are quantitatively the same for the $x=0.010$ and $x=0.067$ samples.

The spin-lattice-relaxation rate ($1/T_1$) is sensitive to the low-frequency fluctuation spectrum of electronic spin excitations in magnetic systems. In UBe_{13} and other heavy-fermion systems, $1/T_1$ exhibits the same large enhancement at low temperatures in the low-frequency excitations that is responsible for the characteristically large electronic specific heat observed in these materials. We have measured $1/T_1$ for the ^{11}B nucleus in the $x=0.030$ sample at 4 and 77 K and find $1/T_1 = 2.78\pm0.03$ sec^{-1} and 4.25 ± 0.09 sec^{-1}, respectively. For comparison, in pure UBe_{13}; $1/T_1$ of ^{9}Be at 4 and 77 K is approximately 0.60 and 0.96 sec^{-1} respectively.[12] These values differ by less than a factor of 5 in magnitude compared to the borated sample and both show a similar behavior of the product $1/T_1T$. Although little NMR data exist on semiconducting elemental B, the spin-lattice relaxation rate is quadrupolar in nature and the time dependence to the recovery of the magnetization exhibits multiexponential behavior[13] which is unlike our observed single exponential recovery. ^{11}B NMR measurements in UB_2,[14] a potential second phase, show a

Korringa-like behavior and give $1/T_1 \cong 0.01$ sec^{-1} at 4 K, which is three orders of magnitude smaller than what we measure. These comparisons emphasize that the boron we observe probes the heavy-fermion enhancement and does not originate from elemental boron or from a second phase.

IV. CONCLUSION

We present strong evidence from NMR measurements that shows that the boron in $UBe_{13-x}B_x$ is doped exclusively into the cubic Be(I) site.

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