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MAGNETISM IN NEPTUNIUM BORIDES*

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ABSTRACT

Magnetization measurements were performed on NpB_2 , NpB_4 , and NpB_{12} over the temperature range 2–180 K. NpB_2 is ferromagnetic below $T_C = 99.5 \pm 2$ K; NpB_4 anti-ferromagnetic below $T_N = 52.5 \pm 2$ K. These compounds exhibit approximate Curie-Weiss behavior above their ordering temperatures. The corresponding Pu compounds as well as PuB_5 were found not to exhibit magnetic ordering above 2 K. The susceptibility of NpB_{12} is relatively independent of temperature. Attempts to prepare NpB_6 in the arc furnace were unsuccessful. The ferromagnetism of NpB_2 is apparently itinerant in nature, the moment being unsaturable at 52 kOe and 2 K and having magnitude $\sim 0.3 \mu_B$ per Np atom. The very occurrence of magnetism in the compound is somewhat surprising considering the relatively small separation between nearest-neighbor Np atoms in the compound, $d_{\text{Np-Np}} = 3.16 \text{ \AA}$.

INTRODUCTION

Following the discovery¹ that nonmagnetic UB_4 could be made ferromagnetic by alloying with nonmagnetic rare earth tetraborides (UB_4 , LaB_4 , LuB_4), it became of interest to investigate the magnetic properties of the other actinide tetraborides NpB_4 and PuB_4 . We report here the results of studies on these compounds and also studies on NpB_2 , PuB_2 , PuB_6 , and NpB_{12} . The diboride compounds are hexagonal, with alternating layers of actinide (An) and boron atoms; the tetraborides are tetragonal, with an atomic arrangement intermediate between the layered diborides and the cubic hexaborides, the latter possessing a CsCl lattice of An atoms and boron octahedra. The dodecaboride structure consists of a NaCl arrangement of An atoms and boron cubooctahedra.² We were unable to prepare NpB_6 by standard arc-melting techniques.³ No attempt was made to prepare PuB_{12} .

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EXPERIMENTAL

The alloys were prepared by melting together in a He-Ar arc furnace appropriate amounts of An metal and boron pellets. Magnetic measurements were made before and after annealing in vacuum at 1300°C for 2 hrs. The results obtained were qualitatively similar, but sometimes differed slightly quantitatively. The data employed were those obtained after annealing.

X-ray powder diffraction analyses revealed that all but the tetraboride samples consisted of a major and a minor phase even after heat treatment. Intensity comparisons indicated that the relative amounts of the minor phases (given in parentheses) were as follows: NpB_2 (5% NpO_2), PuB_2 (10% PuB_4), PuB_6 (25% PuB_4), NpB_{12} (10% NpB_4). These values were used to ascertain the magnetic strengths appropriate to the major phases of interest.

The magnetic studies were performed in a Foner-type vibrating sample magnetometer incorporating a superconducting solenoid capable of fields up to 52 kOe.⁴

In the NpB_2 and NpB_4 samples (and perhaps to a very slight extent in NpB_{12}), there was found at all temperatures investigated a weak, easily saturated ferromagnetic component apparently not directly related to the magnetic properties of the phases of interest. This parasitic ferromagnetism has been observed previously in other Np compounds and has been dubbed " σ_0 ."⁵ The origin of σ_0 is not known. In our studies a possible source could be NpC , since our Np metal contained 125-340 ppm C by weight.⁴ NpC is ferromagnetic below 200 K⁶, and, were the C in our starting material present in the alloys as NpC , it could account for the σ_0 values observed by us ($\lesssim 40$ emu/mole Np). In other alloys, however, σ_0 has been observed to persist to room temperature,⁵ so, were C at fault in those cases, it would have to exist in a more complex form.

Corrections for demagnetizing effects were small in all the alloys studied and were ignored.

RESULTS

NpB_2 . The magnetization of NpB_2 as a function of applied field--determined at several representative temperatures between 2 and 180 K--is shown in Fig. 1. The curves generated are qualitatively similar to those obtained for the traditional itinerant ferromagnets ZrZn_2 and Sc_3In and the apparently itinerant NpOs_2 .⁵ To be noted are 1) the finite slope of M vs. H even at high fields and low tempera-

tures, and 2) the small value of the induced moment ($\sim 0.3 \mu_B$ per Np atom) even at $H = 52$ kOe and $T = 2$ K. It seems likely that NpB_2 is an itinerant ferromagnet, although an unequal local-moment ferrimagnetic or similarly complex configuration would not seem necessarily ruled out by the present data. We indicate below that itinerancy is probably more compatible with the interatomic spacing between Np atoms in the compound.

Generally, magnetizing and demagnetizing curves were almost indistinguishable above a few kOe of applied field. The remanence of $\sim 0.14 \mu_B$ per Np atom for the 2.2 K trace is illustrated in Fig. 1.

In the paramagnetic region $1/\chi$ was approximately linear with T between 140 and 180 K, yielding the tentative Curie-Weiss parameters $\mu_{\text{eff}} \sim 1.7 \mu_B$ per Np atom and $\theta_p \sim 82$ K. The parasitic σ_0 was subtracted out in this region by a conventional χ vs. $1/H$ plot, treating σ_0 as a ferromagnetic impurity.

In the ferromagnetic region, σ_0 was eliminated by the following approximate method. The sample was cooled in zero field to the desired temperature, and the observed spontaneous moment subtracted as a field-independent quantity from the ensuing magnetization curve. This technique yielded Arrott plots of reasonable linearity in the vicinity of T_C , which was determined to be 99.5 ± 2 K.

NpB_4 . The susceptibility of NpB_4 is shown as a function of temperature in Fig. 2. The peak in χ at 52.5 K is characteristic of a transition into an antiferromagnetic state. Between 80 and 140 K, a Curie-Weiss fit to the data yielded $\mu_{\text{eff}} \sim 1.4 \mu_B$ per Np atom and $\theta_p \sim -30$ K. σ_0 was subtracted from the data as described above for the paramagnetic region of NpB_2 .

PuB_2 , PuB_4 , PuB_6 , and NpB_{12} . The magnetic susceptibilities of these compounds were found to be relatively independent of temperature and of magnitudes ($\times 10^{-4}$ emu/Oe mole): PuB_2 : 4.2, PuB_4 : 7.2, PuB_6 : 15.9, NpB_{12} : 9.8. Because of the technique used to determine the amounts of each phase in the two-phase samples, the numbers for all but PuB_4 should be regarded as accurate to no more than $\pm 25\%$. Also, because of the limited sensitivity of the magnetometer, the "temperature independence" of χ for these compounds is meant to imply a variation of no more than $\pm 20\%$ between 2 and 180 K.

DISCUSSION

The magnetism of NpB_2 and NpB_4 is apparently the first observation of such in binary An-B systems. In discussing the magnetism of these compounds, the most useful reference point is probably UB_4 . The suggested critical (minimum) interatomic An-An spacings for magnetism in U, Np, and Pu compounds are 3.4-3.6, ~ 3.25 , and ~ 3.4 Å, respectively.⁷ With a U-U spacing of 3.71 Å, UB_4 must nevertheless be diluted to be made magnetic.¹ As we have learned, dilution is not necessary for NpB_4 ($d_{\text{Np-Np}} = 3.72$ Å), perhaps because of the smaller proposed critical value. Spacing considerations alone do not explain the absence of magnetism in PuB_4 and PuB_6 , however (nor in PuB_2 , see below), and further studies, including the formation of ternary alloys, are planned to further elucidate the nature of the magnetism in these systems.

The Np-Np spacing in NpB_{12} is very large, and one would be inclined to associate its magnetism with local moment Van Vleck behavior. Troć *et al*, on the other hand, have suggested a band description for the isomorphous UB_{12} .⁸

With an interatomic Np-Np spacing of only 3.16 Å, magnetism (albeit itinerant) was not expected in NpB_2 . Such a small spacing is very close to that in $\alpha\text{-Np}$ itself ($d_{\text{Np-Np}} = 3.11$ Å, ave.).^{7,9} Perhaps only the increased 5f-5f overlap in $\alpha\text{-Np}$ due to a larger coordination number (CN 11-13⁹ compared to CN 6 for NpB_2)² and/or the presence of four very close neighbors in the $\alpha\text{-Np}$ structure ($d < 2.7$ Å⁹) prevents the occurrence in the pure metal of magnetism similar to that in NpB_2 .

It is implicit in the analysis of actinide superconductivity and magnetism on the basis of An-An interatomic spacing⁷ that alloys/compounds with spacings near the critical value for a given element may be expected to possess a marginal character (UPt , e.g.,¹⁰); and the apparently itinerant nature of NpB_2 (and NpOs_2)⁵ are consistent with this description, but the magnitude (~ 100 K) of the Curie temperature of NpB_2 is quite surprising. We are cognizant of the moderately impure nature of our Np starting material, but several consistency aspects of the results obtained make difficult any conclusion other than that the ferromagnetism observed is indeed due to NpB_2 . It would seem that Np metal and Np alloys/compounds are more prone to magnetism than had been expected.

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Fig. 1. Magnetization of NpB_2 at various temperatures.

Fig.2. Magnetic susceptibility of NpB_4 .