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Letter

Specific Heat and TEM Study of the New Layered Boride $PrRh_{4.8}B_2$ Obtained by the Molten Metal Flux Growth

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Specific heat and transmission electron microscope (TEM) measurements were carried out for the $PrRh_{4.8}B_2$ compound which has been identified as having a novel layered structure. TEM measurements on molten metal flux grown single crystals of $PrRh_{4.8}B_2$ confirmed the crystal structure in which additional rhodium layers are inserted into a $CeCo_3B_2$-type structural framework. -[$PrRh_3B_2$]- blocks are separated by partially occupied rhodium metal -[Rh]- layers. Specific heat measurements reveal a magnetic transition occurring in $PrRh_{4.8}B_2$ at T_{mag} = 6.8 K, which is concluded to be a ferrimagnetic transition. Strikingly, this transition temperature is significantly higher than that of the simple $PrRh_3B_2$ compound (T_{mag} = 3.6 K) and there is an indication that we have succeeded in enhancing the properties through the rhodium layer insertion.

Key Words: *$PrRh_{4.8}B_2$*, *Layered Compound*, *Boride*, *TEM*, *Specific Heat*, *Magnetic Transition*

1. Introduction

The rare earth borides have yielded intriguing systems by which to study fundamental problems in physics and chemistry[1,2]. The rare earth rhodium boride system R-Rh-B has attracted increasing attention with recent discoveries of interesting properties of their crystal structure, hardness, magnetism, superconductivity, heavy-electron behavior, valence fluctuation, and catalytic properties[3-11]. For the praseodymium system, two compounds $PrRh_3B$[12] and $PrRh_3B_2$[13] were previously known and investigated. Recently, we have discovered a novel $PrRh_{4.8}B_2$ compound that was obtained by the molten metal flux growth method[14]. This compound was identified as having a novel layered structure and is studied further in the present paper through TEM and an investigation of specific heat which revealed striking behavior.

2. Experimental details

Single crystals of $PrRh_{4.8}B_2$ in the form of a hexagonal plate were grown by the molten metal flux growth method using Cu as flux as described in a previous study[14]. $PrRh_{4.8}B_2$ is orthorhombic with the space group *Fmmm*; a = 0.9697(4) nm, b = 0.5577(2) nm and c = 2.564(3) nm.

In order to observe the layered structure of the $PrRh_{4.8}B_2$ single crystal, cross-sectional TEM observation was employed. Thin specimens for the cross-sectional TEM observation were prepared by ion-milling. Electron diffraction (ED) patterns and high-resolution electron microscopy (HREM) images were obtained using a 200 kV electron microscope (JEM-2010) with a resolution of 1.9 Å.

The specific heat of $PrRh_{4.8}B_2$ was measured using a transient heat pulse method with a small temperature increase of 2 % relative to the system temperature. A crystal with some thickness was selected and attached to an alumina plate holder using Apiezon N grease. The measured temperature region was from 300 K to 1.8 K. The results from a measured blank run of the holder and grease were subtracted from the data to obtain the specific heat of $PrRh_{4.8}B_2$.

3. Results and Discussion

Figure 1 shows (a) a HREM image, (b) the corresponding ED pattern with the incident beam parallel to [210] and (c) the atomic arrangement determined by the single-crystal X-ray diffraction analysis[10]. An arrow in Fig.1(a) indicates the periodicity along the [001] direction. Black, white and gray circles, along with the rectangle drawn by thick lines in Fig.1(c) indicate Pr, Rh and B atoms, and the unit cell, respectively. A stacking structure along the [001] direction can be observed in the present single crystal. Three bright layers as indicated by arrowheads in Fig.1(a) correspond to three Pr layers in the $PrRh_3B_2$-block. On the other hand, the partly-occupied Rh layers, the Kagome nets, between $PrRh_3B_2$-blocks were not clearly observed, because of the low occupation probability of the two Rh sites. The striking feature of the HREM image is that the stacking sequence is well ordered without stacking faults. This feature is consistent with that of the ED patterns, which exhibit sharp diffraction spots.

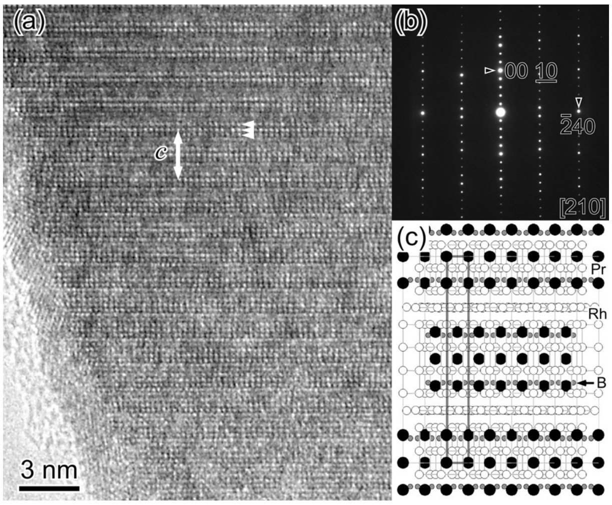

Fig.1 (a) HREM image, (b) the corresponding ED pattern and (c) the crystal structure along the [210] direction. An arrow in (a) indicates the periodicity along the [001] direction. The arrowheads in (a) correspond to the three Pr layers in the $PrRh_3B_2$-block. The black, white and gray circles, and the rectangle drawn by thick lines in (c) indicate Pr, Rh and B atoms, and the unit cell, respectively.

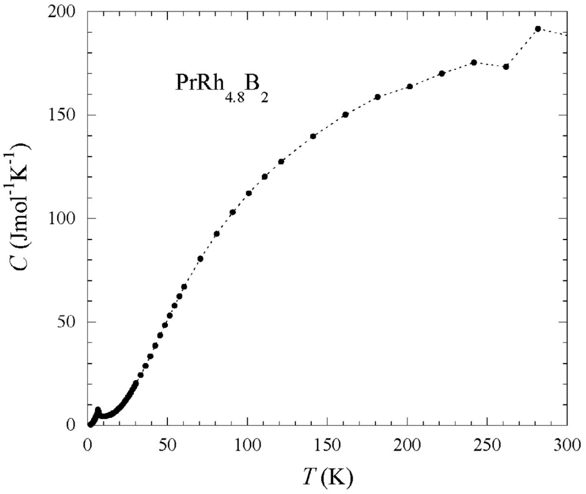

Fig.2 Temperature dependence of the specific heat C of $PrRh_{4.8}B_2$.

The temperature dependence of the specific heat C of $PrRh_{4.8}B_2$ throughout the entire temperature range is plotted in Fig.2. Scattering of the data is observed directly below 300 K, however, this can be attributed to an artifact of the measurement. The specific heat shows general smooth behavior down to the low temperature region where a peak exists. A deviation from the Curie-Weiss law was previously observed in the magnetic susceptibility below 50 K[14]. This is not apparent in the form of any clear anomaly in the specific heat indicating that the deviation is not due to any significant magnetic transition, but instead a possible commencement of short range order.

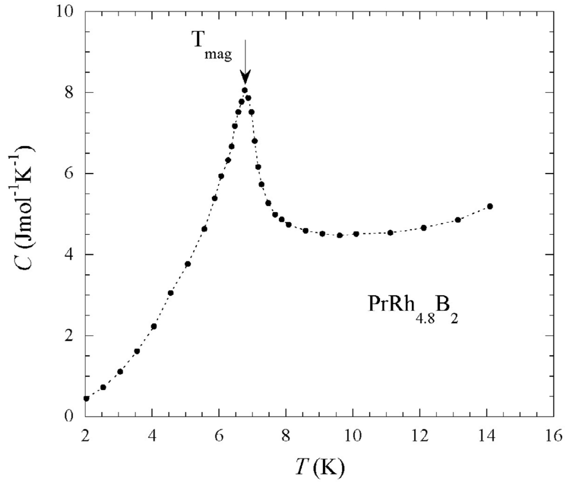

Fig.3 Low temperature specific heat C of $PrRh_{4.8}B_2$.

The low temperature region was measured in detail and plotted in Fig.3. A peak indicative of a magnetic transition is observed at T_{mag} = 6.8 K. The magnetization curve at 4.7 K[14] shows a weak ferromagnetic component, so our results point to a ferrimagnetic transition occurring in $PrRh_{4.8}B_2$ at T_{mag} = 6.8 K. This result is very noteworthy because the structure of $PrRh_{4.8}B_2$ can be described as a novel layered structure formed of -[$PrRh_3B_2$]- blocks separated by partially occupied rhodium metal layers. The compound $PrRh_3B_2$ was first reported to have a simple ferromagnetic transition at T_C = 1.68 K[13]. It was subsequently found that the magnetic ordering is more complex and that $PrRh_3B_2$ is a ferrimagnet with an ordering temperature of T_{mag} = 3.6 K[15] which is much lower than that observed in the present study. Therefore, the magnetism is found to be significantly enhanced in the new $PrRh_{4.8}B_2$ compound, which indicates that the interlayer rhodium atoms have a large effect on the electronic structure of this compound.

It may also be useful to attempt to synthesize a $CeRh_{4.8}B_2$ compound, because $CeRh_3B_2$ has an anomalously high ferromagnetic transition temperature of T_C = 120 K[16]. Any significant increase of this transition temperature through such “material engineering” (i.e. introduction of rhodium atomic layers) would be very exciting.

Finally, $PrRh_{4.8}B_2$ is the first compound discovered of its kind to have been discovered. Therefore a nonmagnetic analog sample does not exist. We will also next try to prepare such a sample, e.g. $LaRh_{4.8}B_2$, in order to enable the determination of the magnetic entropy and clarify the properties of this novel compound.

4. Conclusions

Through the TEM measurements we were able to confirm the well ordered atomic arrangement of $PrRh_{4.8}B_2$, which is a modified $CeCo_3B_2$-type structure, where additional rhodium layers separate -[$PrRh_3B_2$]- blocks. Specific heat measurements reveal a magnetic transition occurring in $PrRh_{4.8}B_2$ at T_{mag} = 6.8 K, which is concluded to be a ferrimagnetic transition. Strikingly, this transition temperature is significantly higher than that of the simple $PrRh_3B_2$ compound (T_{mag} = 3.6 K) indicating that we have succeeded in enhancing the properties through the rhodium layer insertion.

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