Anomalous pressure effect on the Nèel temperature and volume of DyB$_6$

Tetsujiro Eto, Gendo Oomi, Takeshi Sakai, Yoshiya Uwatoko, and Satoru Kunii

Anomalous pressure effect on the Nèel temperature and volume of DyB$_6$

Tetsujiro Eto,[1] Gendo Oomi,[1,a] Takeshi Sakai,[2] Yoshiya Uwatoko,[3] and Satoru Kunii[4]

[1]*Kurume Institute of Technology, 2228-66 Kamitsu-machi, Kurume, Fukuoka 830-0052, Japan*
[2]*National Institute of Technology, Ariake College, 150 Higashihagio-machi, Omuta, Fukuoka 836-8585, Japan*
[3]*Institute of Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*
[4]*Department of Physics, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan*

The pressure effect on the Nèel temperature T_N of DyB$_6$ has been investigated by measuring the temperature dependence of electrical resistivity (ρ) at various pressures up to 8 GPa. It was found that T_N increases almost linearly with pressure in the range of 0-2 GPa and then tends to saturate above 2 GPa. The pressure derivative of T_N below 2 GPa was estimated to be 2.6 K/GPa. The pressure effect on the volume of DyB$_6$ has also been measured at high pressure up to 14 GPa at room temperature using X-ray diffraction and diamond anvil cell. The pressure dependence of volume of LaB$_6$ was also measured for the comparison. It is revealed that DyB$_6$ is more compressible than LaB$_6$. The origin for this observation is suggested to be due to the difference of the ionic size of the rare earth elements, or the strong electron-phonon interaction in DyB$_6$. *© 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5042623

I. INTRODUCTION

There have been a lot of reports for the anomalous properties of lattice compression in rare earth compounds.[1,2] Among them, RB$_6$ compounds (R: rare earth element) with cubic CaB$_6$ structure have been well known to show a wide variety of interesting electronic and magnetic properties depending on R. Among them, DyB$_6$ is a novel Dy compound because of the existence of ferroquadrupolar (FQP) ordered phase and antiferromagnetic (AFM) ordering at low temperature. It shows a structural phase transition at T_Q=30 K from CaB$_6$ to rhombohedral structure accompanied by FQP ordering and AFM transition at T_N=25 K.[3] It is interesting to investigate the interplay between quadrupolar and antiferromagnetic interaction by using pressure as a control parameter. For instance, it has been revealed that the 1st order transition accompanied by structural change at ambient pressure disappeared above 1.2 GPa and then a broad 2nd order like transition was observed around T_Q at high pressure.[4] Possibly the interplay between AFM and FQP is complicated at high pressure. Since the lattice properties of DyB$_6$ are dominated by the strong electron–phonon interaction,[5,6] an anomalous lattice compression of DyB$_6$ may be observed under high pressure. In the present work we measured electrical resistance of DyB$_6$ under high pressure. The pressure dependence of volume is also measured to clarify the crystal structure at high pressure and the relation between elastic properties and magnetic ordering temperature.

II. EXPERIMENTAL

Single crystalline DyB$_6$ was prepared by the crucible-free vertical floating zone method.[7] Electrical resistivity under high pressures was measured using a standard dc four-probe method with

---

^{a}Corresponding author. e-mail: geomi@kurume-it.ac.jp.

electrical current applied in the (110)-plane in the temperature range from 4.2 K to room temperature. Hydrostatic pressures up to 8 GPa were generated by using a cubic anvil press. A 1:1 mixture of Fluorinert, FC70 and 77 was used as a pressure transmitting medium. High pressure X–ray diffraction was performed by using a diamond anvil cell with SUS-301 as a gasket. The pressure transmitting medium was a 4:1 mixture of methanol and ethanol alcohol. The observation was carried out in the range of approximately hydrostatic conditions at room temperature. The X-ray diffraction measurement was done by using an angle resolved method with MoKα radiation and a 2-dimensional x-ray detector from PILATUS 200K (DECTRIS). The observed powder X-ray diffraction patterns both of LaB_6 and DyB_6 indicate that these sample are single phase and have a CsCl-type structure at ambient pressure.

III. EXPERIMENTAL RESULTS

A. Nèel temperature T_N at high pressure

Fig. 1 shows the temperature dependence of the electrical resistivity $\rho(T)$ at various pressures up to 8 GPa. At ambient pressure, $\rho(T)$ decreases smoothly with decreasing temperature, and shows a small discontinuity around 30 K ($=T_Q$) due to the quadrupolar ordering of Dy ions that accompanied by the lattice distortion. Furthermore, the $\rho(T)$ shows a pronounced peak followed by a rapid decrease below 25 K ($=T_N$) due to the antiferromagnetic ordering. The behavior in the $\rho(T)$ curve at ambient pressure is in good agreement with that reported previously.[8] It should be noted, however, that an increase of the magnitude of temperature derivative in the $\rho(T)$ curve below 100 K is enhanced as it approaches T_Q. This behavior of $\rho(T)$ curve is a common feature for HoB_6 as well as DyB_6 in which the elastic softening in C_{44} and C_L mode was observed above T_Q by the sound velocity measurement,[9] and the softening and kink features of the phonon dispersion were also detected just above T_Q in DyB_6 by an inelastic X-ray scattering (IXS) measurement.[5,6,10] These features have been interpreted as consequence of a strong electron-phonon interaction for the large-amplitude motion of the heavy rare earth ions in a hard cage composed of boron atoms. This fact indicates the scattering of conduction electrons from localized vibrational mode plays an important role in the electrical properties in these compounds.

Application of pressure gives rise to an overall decrease of the resistivity in the temperature range from 4.2 K to 300 K, as shown in Fig. 1. As pressure increases, the resistivity anomaly near T_Q is quickly smeared out, and the peak of $\rho(T)$ at T_N becomes less prominent. The temperature derivative $\partial\rho/\partial T$ above T_Q rapidly decreases with pressure, which is expected to be a result of reduction in the scattering of conduction electrons by local phonons. Since the magnitude of $\partial\rho/\partial T$ is related to the phonon softening,[9] this result may indicate a decrease of the softening in DyB_6 under pressure. A pressure-induced crossover like as $CeAl_2$ was not observed below 8 GPa.
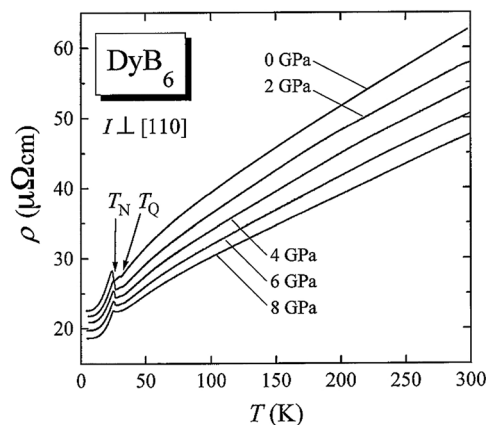

FIG. 1. Temperature dependence of the electrical resistivity for DyB_6 at various pressures.
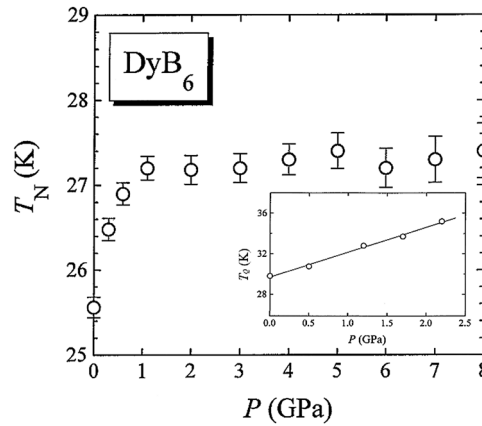
FIG. 2. Pressure dependence of the Néel temperature of DyB_6 at various pressures. The inset shows the pressure dependence of quadrupole ordering temperature T_Q.

Fig. 2 shows the pressure dependence of the Néel temperature T_N, which was determined from the inflection temperature in the $\rho(T)$ curve, as is shown in the Fig. 1. T_N is found to increase with increasing pressure. This reflects a gradual enhancement of the RKKY interaction among well local-ized 4f moments in Dy ions. The pressure derivative of T_N is estimated to be $\partial T_N/\partial P = 2.6\,\text{K/GPa}$. This value is comparable with the value of 3.6 K/GPa,[4] estimated from the Ehrenfest's relation. In high pressure region above 2 GPa, however, it should be noticed that the pressure dependence of T_N tends to saturate. The pressure dependence of T_Q, which was obtained from thermal expansion measurement, is also shown for comparison.[4]

B. Pressure dependence of volume

The volume compression curves both of LaB_6 and DyB_6 at room temperature are shown in Fig. 3, in which the relative changes in volume, V/V_0 are illustrated as a function of pressure, where V and V_0 are the volume at pressure P and ambient pressure, respectively. It is obviously found that DyB_6 is more compressible than LaB_6 below ~2 GPa. and becomes harder than LaB_6 above ~2 GPa. As the compression curve seems to be difficult to fit to an equation of state in the overall range between 0 and 14 GPa, we tentatively tried to fit the data of DyB_6 in the range 0-2 GPa and in the range 2-14GPa to the following Murnaghan's equation of state, separately:
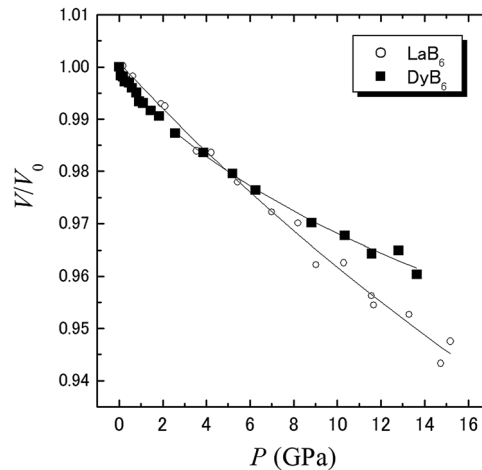

FIG. 3. Relative volume compression V/V_0 with pressure both of LaB_6 and DyB_6. The solid curves are guides of the eye.

TABLE I. Bulk moduli B_0 and their pressure derivatives B_0' of LaB_6, DyB_6.and $CeAl_2$.

	B_0	B_0'
LaB_6 (0-15 GPa)	220	6
DyB_6 (0-2 GPa)	132	86
DyB_6 (2-14 GPa)	215	27
$CeAl_2$ (0-15 GPa)[11]	66	3.3

$$\frac{V}{V_0} = \left(P\left(\frac{B_0'}{B_0}\right) + 1 \right)^{-\frac{1}{B_0'}}, \tag{1}$$

where B_0 and B_0' are the bulk modulus and its pressure derivative at ambient pressure, respectively. The compression curve of LaB_6 is found to fit well to equation (1) by using two parameters B_0 and B_0'.

In Table I, B_0 and B_0' of DyB_6 and LaB_6 are listed. We obtained the bulk modulus as B_0=132 GPa below 2 GPa, which is about 40% smaller than 215 GPa for the range 2-14 GPa of DyB_6 and 220 GPa for the range 0-15 GPa of LaB_6. It should be noted that the value of B_0 of DyB_6 in the range 2-14 GPa is roughly the same as that of LaB_6. The values of B_0' of DyB_6 are extremely larger than that of LaB_6. For the comparison the B_0 and B_0' of $CeAl_2$[11] are also listed in Table I, in which B_0'($CeAl_2$) is smaller than these of DyB_6. It was reported that $CeAl_2$ shows a pressure-induced valence transition.[11] The extremely large value of B_0' of DyB_6 suggests that no such transition occurs at high pressure. A possible reason for the anomalous large value of B_0' for DyB_6 below 2 GPa is considered as a consequence that the B cage surrounding Dy ion is squashed by an application of pressure, which is due to the difference in the ionic radius between Dy and La., i.e., in DyB_6 the space for the dynamic motion of Dy ion is larger than that of LaB_6. Then Dy ion has wider space allowing rattle inside B cage than La ion. Furthermore it is expected that the dynamic motion of Dy ions in B cage is rapidly suppressed by applying pressure. On the other hand, a strong electron–phonon interaction has been reported for DyB_6[5,6,10] but not for LaB_6. This difference may be another reason for anomalous compression of DyB_6. At present, it is difficult to determine which is dominant.

IV. DISCUSSION

A. Possible origins for the anomalous pressure effect on T_N

The T_N observed in forgoing section at ambient pressure corresponds to the phase transition in orthorhombic phase. We have revealed that the structural transition at T_Q below 1.2 GPa is different from that above 1.2 GPa by the thermal expansion measurement of DyB_6 under pressure.[4] The change in the length along [111] direction at T_Q at ambient pressure is observed to be smeared out at 2.2 GPa. This finding suggests that the structural change from cubic to rhombohedral disappears at high pressure below 2 GPa, indicating structural instability. This fact indicates that around 2 GPa, the crystal structure may be cubic or a mixed phase of cubic and orthorhombic. Then around 2 GPa, it is difficult to say in which phase the antiferromagnetic transition occurs. The result in Fig. 2 suggests that the T_N in rhombohedral phase increases with pressure but that in other phases may show small or negligible pressure effect.

B. Volume anomaly in DyB_6

The difference of pressure dependence on the volume between DyB_6 and LaB_6 was obtained as ΔV (=V (LaB_6)–V (DyB_6)), as shown in Fig. 4. It is seen that ΔV indicates a small peak at approximately 1.2 GPa, and monotonically decreases with increasing pressure. This phenomenon can be related to previous results of thermal expansion measurements:[4,12] the thermal expansion at T_Q along the cubic [110] axis and $\alpha_{[110]}(T_Q)$ have a peak around 1.2 GPa. It is interesting to note that the anomaly in ΔV in Fig. 4 at room temperature corresponds well with this anomaly at low temperature. But the origin for this finding is not clear at present.
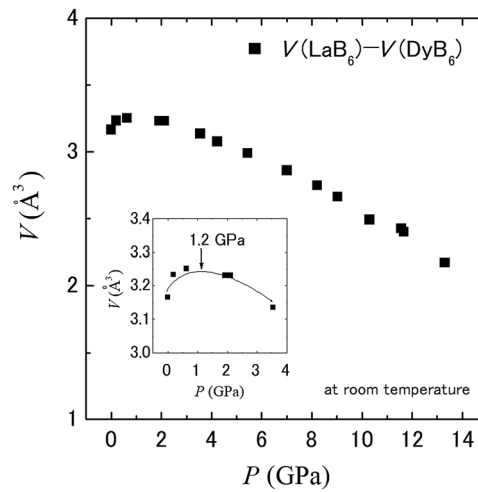
FIG. 4. The difference of volume ΔV (=V (LaB$_6$)–V(DyB$_6$)) as a function of pressure. The inset is enlarged one at pressure range 0-4 GPa. A solid curve is guide of the eye.

In conclusion, we have investigated the pressure effects on the Nèel temperature and the volume of DyB$_6$. It was found that T_N increases almost linearly with pressure below 2 GPa and then tends to saturate above 2 GPa. It is suggested that this anomalous pressure dependence is due to a complicated relation between the crystal structure at low temperature and antiferromagnetic ordering. The volume of DyB$_6$ decreases rapidly below 2 GPa, and the change becomes to be small above 3 GPa, while the compression curve of LaB$_6$ is normal and well fit by an equation of state. It may be possible to say that these results are related to the difference of the ionic size of the rare earth elements, or the strong electron-phonon interaction in DyB$_6$.

[1] M. Ohmura, K. Sakai, T. Nakano, H. Miyagawa, G. Oomi, I. Sato, T. Komatsubara, H. Aoki, Y. Matsumoto, and Y. Uwatoko, J. Magn. Soc. Jpn. **33**, 31 (2009).
[2] G. Oomi, T. Eto, T. Okada, and Y. Uwatoko, Physica B **536**, 293 (2018).
[3] S. Kunii, J. Alloys. Compd. **193**, 292 (1993).
[4] T. Sakai, G. Oomi, and S. Kunii, Physica B **259-261**, 904 (1999).
[5] K. Iwasa, K. Kuwahara, Y. Utsumi, K. Saito, H. Kobayashi, T. Sato, M. Amano, T. Hasegawa, N. Ogita, M. Udagawa, S. Tsutsui, and A. Q. R. Baron, J. Phys. Soc. Jpn. **81**, 113601 (2012).
[6] K. Iwasa, M. Amano, N. Nakao, and Y. Murakami, JPS Conf. Proc. **3**, 016026 (2014).
[7] S. Kunii, J. Phys. Soc. Jpn. **57**, 361 (1988).
[8] K. Segawa, A. Tomita, K. Iwashita, M. Kasuya, T. Suzuki, and S. Kunii, J. Magn. Magn. Mater. **104-107**, 1233 (1992).
[9] S. Nakamura, T. Goto, S. Kunii, K. Iwashita, and A. Tamaki, J. Phys. Soc. Jpn. **63**, 623 (1994).
[10] K. Iwasa, F. Iga, A. Yonemoto, Y. Otomo, S. Tsutsui, and A. Q. R. Baron, J. Phys. Soc. Jpn. **83**, 094604 (2014).
[11] H. Miyagawa, G. Oomi, M. Ohashi, I. Satoh, T. Komatsubara, M. Hedo, and Y. Uwatoko, Phys. Rev. B **78**, 064403 (2008).
[12] Y. Uwatoko, H. Takahashi, and G. Oomi, *Handbook on the Phys. and Chem. of Rare Earths* vol. 51, Chapt. 295 (2017).