Journal of Solid State Chemistry **154,** 275–279 (2000)
doi:10.1006/jssc.2000.8849, available online at http://www.idealibrary.com on IDEAL®

Phonon and Specific Heat Analyses in Rare-Earth Hexaborides

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Received September 9, 1999; in revised form December 28, 1999; accepted January 2, 2000

Systematic analyses of the specific heat of rare-earth hexaborides are presented using phonon data. Similarity of phonon dispersion curves at lower frequency is found for the rare-earth hexaborides. By this fact, it becomes possible to deduce unknown phonon dispersion curves. We can calculate the phonon specific heat precisely using phonon dispersion curves. Magnetic entropy is derived for GdB_6, TbB_6, DyB_6, and HoB_6, indicating their magnetic ground states which are consistent with a point-charge model developed by K. R. Lea *et al.* (1962, *J. Phys. Chem. Solids* 23, 1381). © 2000 Academic Press

INTRODUCTION

Rare-earth hexaborides with a simple cubic CaB_6-type structure have been attracting much attention because of their variety of electronic and magnetic properties (1–3). There have been few studies on heavy rare-earth (Tb, Dy, and Ho) hexaborides, one of the reasons for this being that their incongruent melting property makes it difficult to grow a large single crystal. We have succeeded in growing such large single crystals by a crucible-free floating zone method. The specific heat data of TbB_6, DyB_6, and HoB_6 have already been reported by us (4). However, the magnetic entropy has not yet been obtained. Because the specific heat of LaB_6 for the phonon standard in the rare-earth hexaboride series is too small at low temperature to subtract the phonon part for the above compounds, their magnetic entropy exceeds the theoretical maximum value.

We have developed a new method of specific heat analyses using phonon dispersion curves (5, 6). If we know the phonon dispersion curve, we can calculate the phonon density of states so as to determine the phonon energy. The phonon specific heat can be calculated precisely as the temperature derivative of the phonon energy. The purpose of the present paper is to present systematic analyses of the specific heat of rare-earth hexaborides using phonon data obtained to date.

RESULTS AND DISCUSSION

The phonon dispersion curves obtained by neutron inelastic scattering experiments have been reported so far for LaB_6 (7), CeB_6 (6), and SmB_6 (8). The phonon dispersion curves for the above three compounds are similar, as shown in Figs. 1a and 1b, in which the phonon frequency is converted to Kelvin for the easy comparison with the specific heat data. The phonon dispersion curves for CeB_6 are plotted in Fig. 1a by circles. For LaB_6, shown by $\times$, the frequency of a vertical line is reduced by a frequency reducing factor N ($= 0.985$) so as to coincide with that of CeB_6. Figure 1b shows the same handling for SmB_6 ($\bigcirc$) as for LaB_6 ($\times$) using $N = 0.88$ for the best coincidence. The coincidence between $\bigcirc$ and $\times$ is good in both figures. Surprisingly, the frequency reducing factor N obtained above is the same value as the ratio of the Debye temperature $\Theta(CeB_6 \text{ or } SmB_6)/\Theta(LaB_6)$, which is listed in Table 1. The Debye temperature is calculated by two methods, that is, Houston's method (9) and the mean sound velocities' method (10), using elastic constants C_{44}, C_{11}, and C_{12} obtained by us (11). Two calculation methods give approximately the same values. The above coincidence means that if we know the starting slope of the dispersion curve (that is, at $q = 0$), we may be able to estimate the whole dispersion curve in rare-earth hexaborides. For example, we do not know the phonon structure of YbB_6. However, using the Debye temperature ratio 0.69 for YbB_6, we can fit the specific heat of YbB_6 (7) by that of LaB_6 as shown in Fig. 2.

In Table 1, values for $A = 2C_{44}/(C_{11} - C_{12})$ are shown. Value A is a measure of the elastic anisotropy of the crystal (9). For heavy rare-earth hexaborides (GdB_6–HoB_6), the deviation of A from the value of LaB_6 is large as shown in the table. In these cases the Debye temperature obtained from the elastic constants may be incorrect because of the assumption of Houston's method (9). Therefore, to correct the reducing factor N for heavy rare-earth hexaborides, we have performed neutron inelastic measurements on $Dy^{11}B_6$ to obtain its dispersion curves (12). It has a shape similar to that of LaB_6 and yields $N = 0.58$. It can be noticed that the elastic constant C_{44} and the reducing factor N are related

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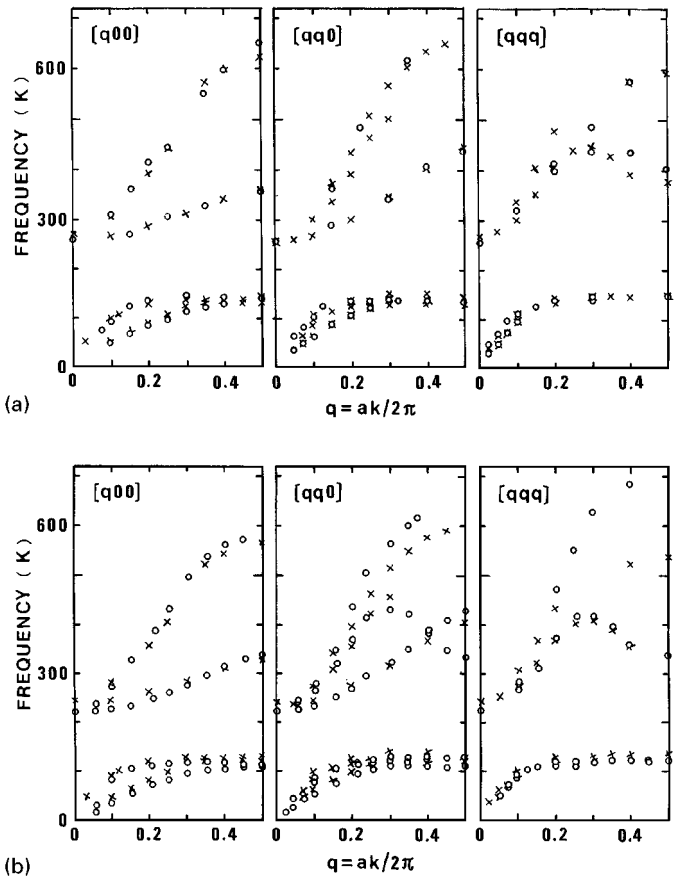

FIG. 1. (a) Phonon dispersion relation for CeB_6 (○) and for LaB_6 (×) in which the frequency is reduced by $N = 0.985$. (b) Phonon dispersion relation for SmB_6 (○) and for LaB_6 (×) in which the frequency is reduced by $N = 0.888$.

empirically. In Fig. 3, we plot the relation between C_{44} and N for LaB_6, CeB_6, SmB_6, and DyB_6. From this figure, we can deduce the value of N for GdB_6, TbB_6, and HoB_6. For

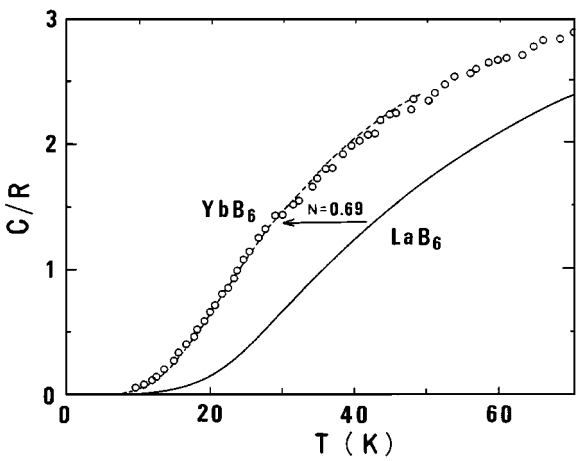

FIG. 2. Specific heat of YbB_6 (○, measured), solid line for LaB_6. The dotted line is obtained from that of LaB_6 using the Debye temperature ratio 0.69.

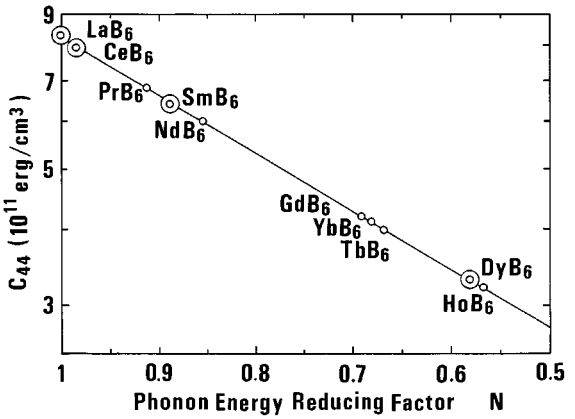

FIG. 3. Elastic constant C_{44} (log scale) versus phonon energy reducing factor N.

GdB_6, we can solve the long-standing problem of its enormous entropy. Using this N value of 0.69, we can estimate much larger phonon specific heat at lower temperature for GdB_6 (13), as shown in Fig. 4a. Then we can obtain the entropy of Rln 8 as is expected theoretically for GdB_6 ($4f = 7$, $^8S_{7/2}$) which is shown in Fig. 4b.

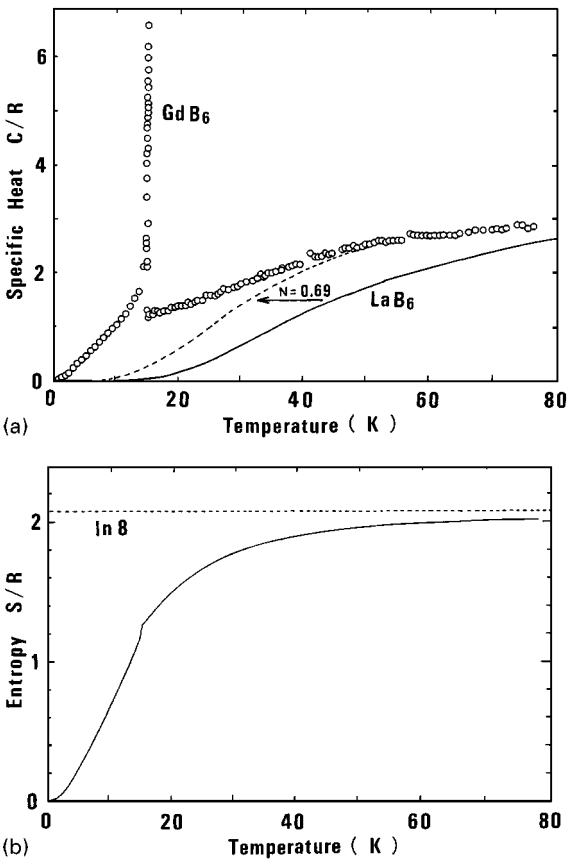

FIG. 4. (a) Specific heat of GdB_6 (○, measured), solid line for LaB_6. The dotted line is obtained from that of LaB_6 using reducing factor 0.69. (b) Magnetic entropy S/R of GdB_6.

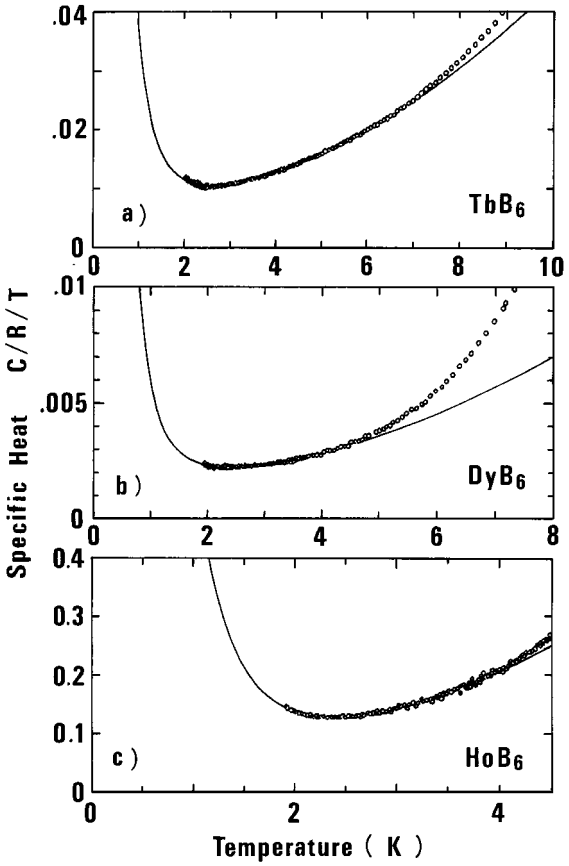

FIG. 5. Specific heat C/R/T at low temperature for (a) TbB_6, (b) DyB_6, and (c) HoB_6. Solid lines are fitted to $C = \alpha/T^2 + \beta T^3 + \gamma T + C_{mag}$, where α, β, and γ are parameters (see text).

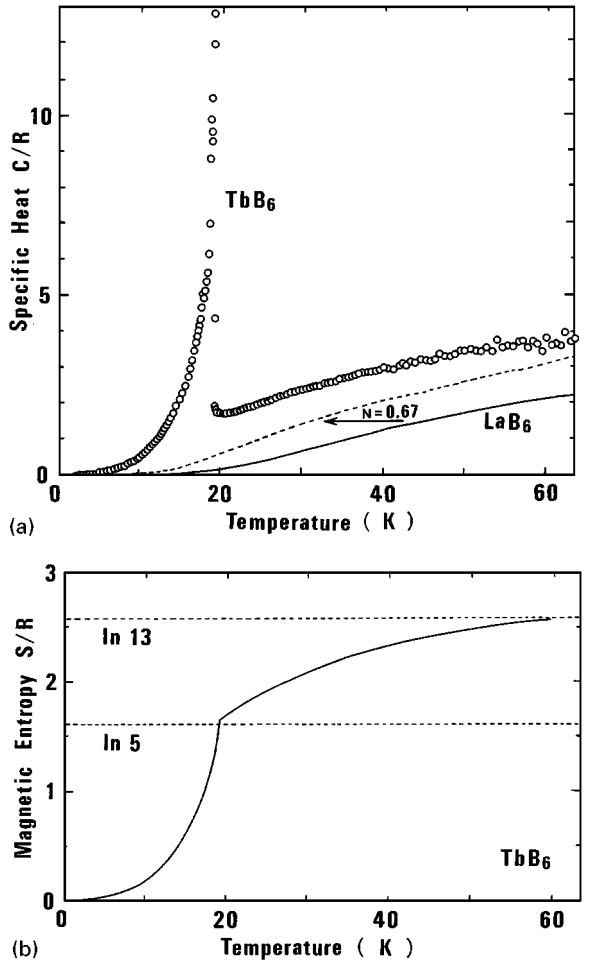

FIG. 6. (a) Specific heat of TbB_6 (○, measured), and solid line for LaB_6. The dotted line is obtained from that of LaB_6 using reducing factor 0.67. (b) Magnetic entropy S/R of TbB_6.

In TbB_6, DyB_6, and HoB_6 at low temperature, the increase of the specific heat with decreasing temperature can be observed as shown in Figs. 5a, 5b, and 5c. At low temperature the specific heat increases with decreasing temperature nearly as $1/T^2$ dependence expected for the nuclear Schottky contribution. Therefore, we assume the specific heat, $C = \alpha/T^2 + \beta T^3 + \gamma T + C_{mag}$. α is the nuclear Schottky specific heat coefficient, β is the phonon and the antiferro spin wave specific heat coefficient which is nearly two orders of magnitude smaller than the total value in the present temperature range, and γ is the electronic specific heat coefficient. C_{mag} is the magnetic specific heat that we want to finally obtain. We attempt to fit the specific heat data by the above formula using α, β, and γ as parameters. The fitting curves are shown by the solid lines in Figs. 5a, 5b, and 5c. For TbB_6, $\alpha = 262$ mJ·K/mol, $\beta = 3.2$ mJ/mol·K^4, and $\gamma = 49.9$ mJ/mol·K^2. For DyB_6, $\alpha = 37.9$ mJ·K/mol, $\beta = 0.73$ mJ/mol·K^4, and $\gamma = 11.5$ mJ/mol·K^2. For HoB_6, $\alpha = 4530$ mJ·K/mol, $\beta = 87.9$ mJ/mol·K^4, and $\gamma = 207$ mJ/mol·K^2. The α values obtained above do not deviate from that of rare-earth metals of Tb, Dy, and Ho (14). After the above correction of the specific heat data, phonon correction is done as described above at higher temperature. Figures 6a, 7a, and 8a show the phonon correction for

TABLE 1
Elastic Constants C_{44}, Elastic Anisotropy Factor A, Debye Temperature Θ and Its Ratio, and Energy Reducing Factor N

	C_{44} (erg/cm^3)	A $(2C_{44}/(C_{11}-C_{12}))$	Θ (K)	Θ (RB$_6$)/Θ (LaB$_6$)	N
LaB_6	8.3×10^{11}	0.384	396	1	1
CeB_6	7.9×10^{11}	0.356	390	0.985	0.985
SmB_6	6.4×10^{11}	0.287	351	0.888	0.888
YbB_6	4.1×10^{11}	0.270	274	0.69	(0.68)
GdB_6	4.2×10^{11}	0.193	—	—	(0.69)
TbB_6	4.0×10^{11}	0.180	—	—	(0.67)
DyB_6	3.3×10^{11}	0.145	—	—	0.58
HoB_6	3.2×10^{11}	0.133	—	—	(0.57)

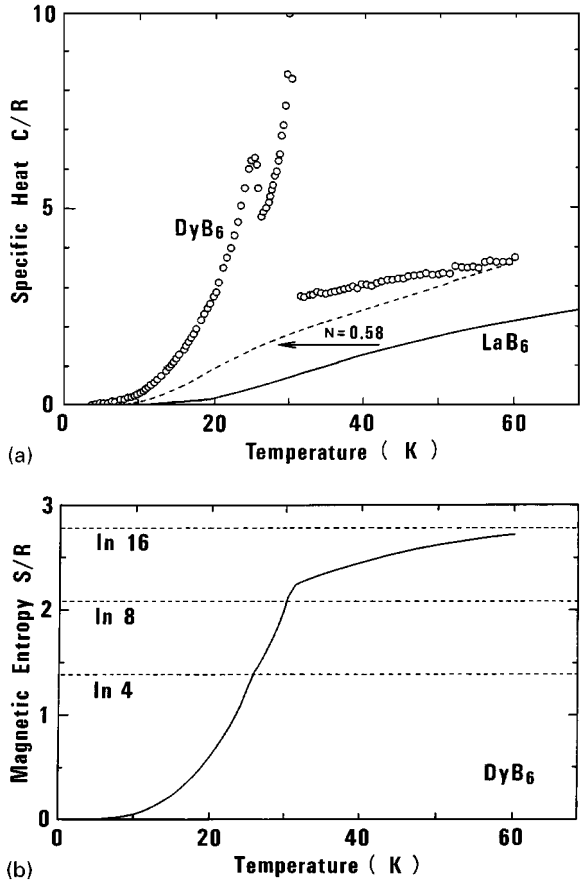

FIG. 7. (a) Specific heat of DyB_6 (○, measured), and solid line for LaB_6. The dotted line is obtained from that of LaB_6 using reducing factor 0.58. (b) Magnetic entropy S/R of DyB_6.

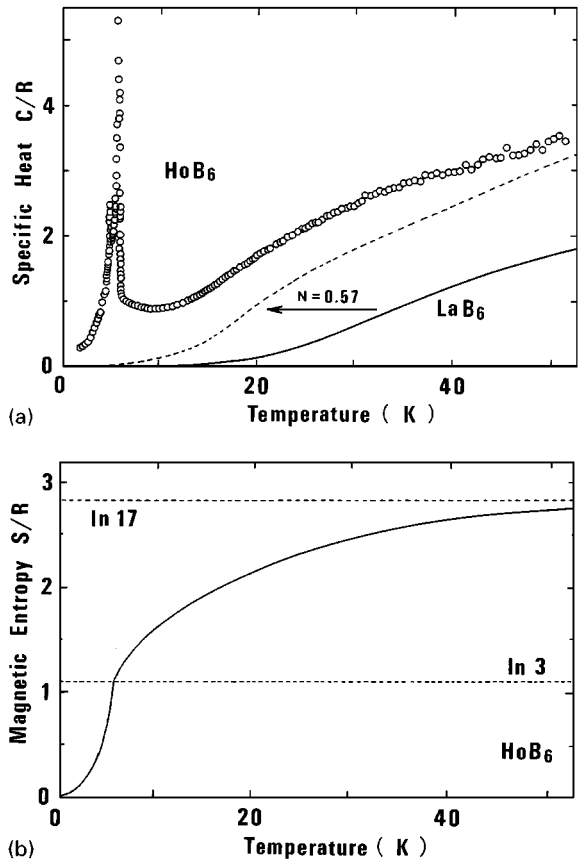

FIG. 8. (a) Specific heat of HoB_6 (○, measured), solid line for LaB_6. The dotted line is obtained from that of LaB_6 using reducing factor 0.57. (b) Magnetic entropy S/R of TbB_6.

TbB_6, DyB_6, and HoB_6, respectively. Figures 6b, 7b, and 8b show the magnetic entropy. They do not exceed their expected theoretical entropy values for Tb^{3+} ($J = 6$), Dy^{3+} ($J = 15/2$), and Ho^{3+} ($J = 8$).

We use the values of C_{44} obtained at room temperature in above analyses. C_{44} values at temperatures higher than the critical point (magnetic or quadrupole transition temperature) for rare-earth hexaborides do not deviate so much from the room temperature value (11). Moreover phonon specific heat is not important at low temperature, and specific heat reflects the causes of energy ε at the temperature T so as to $\varepsilon/kT \sim 3$, where k is the Boltzman constant (15). Therefore, it is possible to use the room temperature values of C_{44} in our analysis.

The magnetic ground states of PrB_6 and NdB_6 have been determined by the neutron inelastic scattering measurements (16, 17). Their level schemes and their relative splittings are consistent with the point charge model by Lea *et al.* (18). The level schemes for TbB_6, DyB_6, and HoB_6 seem to be in the same situation as above. In TbB_6, the entropy is Rln 5 at the magnetic transition temperature seen in Fig. 6b. The ground state is Γ_3 (two-fold degeneracy), and next Γ_5 (three-fold deg.) from Ref. (18), and consistent with the entropy at the magnetic transition temperature. In DyB_6, the entropy is Rln 4 at the Neel temperature and Rln 8 at the quadrupolar transition temperature. The ground state is $\Gamma_8^{(1)}$ (four-fold deg.) and $\Gamma_8^{(2)}$ (four-fold deg.), consistent with the entropy. In HoB_6, the entropy is Rln 3 at the magnetic transition temperature. The ground state is $\Gamma_5^{(2)}$ (three-fold deg.), also consistent with the entropy. More detailed calculations and discussions of crystal field parameters for magnetic rare-earth hexaborides will be described in a forthcoming paper.

CONCLUSION

We found a similarity of phonon dispersion curves among the rare-earth hexaborides. Using this fact, we were able to deduce the phonon structure of all rare-earth hexaborides. Systematic analyses of the specific heat of rare-earth hexaborides were performed. Magnetic entropy was derived for GdB_6, TbB_6, DyB_6, and HoB_6 for the first time.

ACKNOWLEDGMENTS

We are very grateful to Prof. T. Goto, Prof. M. Motokawa, and Assoc. Prof. H. Nojiri for helpful discussions. This work was supported by a Grant-in-Aid from the Japanese Ministry of Education, Science, and Culture.

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