ULTRASONIC INVESTIGATION
OF ANTIFERROQUADRUPOLE ORDERINGS
IN HoB₂C₂ AND DyB₂C₂*

TERUTAKA GOTO, TATSUYA YANAGISAWA, KOICHIRO HYODO
YUICHI NEMOTO

Graduate School of Science and Technology, Niigata University
Niigata 950-2181, Japan

SHINGO MIYATA, RYUTA WATANUKI AND KAZUYA SUZUKI

Graduate School of Engineering, Yokohama National University
Yokohama 240-8501, Japan

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The antiferroquadrupole orderings of the ternary rare earth compounds HoB₂C₂ and DyB₂C₂ have been investigated by means of ultrasonic measurements. The transverse \((C_{11} - C_{12})/2\), \(C_{44}\), \(C_{66}\) modes in HoB₂C₂ exhibit characteristic softening above \(T_{c2} = 5.0\) K, which consist with an \(E\)-doublet and a singlet for the ground state. Considerable elastic softening and ultrasonic attenuation in phase IV below \(T_{c1} = 5.9\) K of HoB₂C₂ indicates an enhancement of the quadrupole fluctuation with a relaxation rate \(\tau = 7 \times 10^{-9}\) sec. A softening of the transverse elastic constant \(C_{44}\) in DyB₂C₂ above \(T_Q = 24.7\) K indicates accidentally degenerated Kramers doublets of \(E_{1/2}\) and \(E_{3/2}\) for the ground state.

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The orbital as well as spin degrees of freedom in localized 4\(f\)-electron system of rare earth compounds give rise to competitive inter-site interaction between the electric quadrupole moment and magnetic dipole moment. The 4\(f\)-electron compounds with an orbital degenerated ground state in particular favor the quadrupole ordering in addition to magnetic ordering at low temperatures. It is now recognized that CeB₆ with \(I₈\) ground state in a cubic lattice shows antiferroquadrupole (AFQ) ordering of \(O_{yz}\), \(O_{zx}\) and \(O_{xy}\).

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Yamaguchi et al. have reported that DyB$_2$C$_2$ with a tetragonal LaB$_2$C$_2$-type structure transits into AFQ phase II at $T_Q = 24.7$ K and successively changes to antiferromagnetic (AFM) phase III at $T_N = 15.3$ K [2, 3]. A $\lambda$-type anomaly in specific heat and little change in magnetic susceptibility around $T_Q$ mean the AFQ ordering in phase II. Resonant X-ray scattering showed successfully the AFQ ordering below $T_Q$ in DyB$_2$C$_2$ [4]. Onodera et al. have recently found that the isomorphous compound HoB$_2$C$_2$ has an interest magnetic phase diagram consisting of the AFQ phase II, AFM phase III and an ordered phase IV [5]. The tilted angle of the magnetic moment in the basal plane in phase III of both compounds is accounted for the coexistence of the antiferro-ordering of magnetic and quadrupole moments. It is of quite interest that the phase IV in HoB$_2$C$_2$ locates at a tetra-critical point, where two different types of intersite interaction of quadrupole and magnetic moments compete each other. It is worthwhile to refer the magnetic phase diagram of Ce$_{0.75}$La$_{0.25}$B$_6$ [6]. Diffuse scattering by neutron experiments in phase IV of HoB$_2$C$_2$ is distinguished from the appreciable magnetic Bragg peaks in phase III. In the present paper, we show ultrasonic investigation on HoB$_2$C$_2$ and DyB$_2$C$_2$. Taking into account the elastic softening of shear modes, models for the ground state with orbital degeneracy in both compounds are argued. Ultrasonic attenuation in phase IV is presented.

Single crystals with lamella shape were grown by a tetra-arc furnace. Piezoelectric LiNbO$_3$ plates were bonded on the plane parallel surfaces of the specimen prepared by a discharge cutter. The sound velocity $v$ was measured by a phase comparator based on mixer technology. In a calculation of the elastic constants $C = \rho v^2$ we employ the mass density $\rho = 6.83 \times 10^2$ g/m$^3$ for HoB$_2$C$_2$ and $\rho = 6.82 \times 10^2$ g/m$^3$ for DyB$_2$C$_2$. The transverse mode was available for $(C_{11} - C_{12})/2$, $C_{44}$, and $C_{66}$.

Fig. 1 shows the temperature dependence of the elastic constant $C_{44}$ of HoB$_2$C$_2$. It is remarkable that $C_{44}$ shows a softening of about 22% below 100 K. Other shear modes show also the softening of 2.4% in $(C_{11} - C_{12})/2$ and of 5.5% in $C_{66}$ [7]. These softening of shear modes are referred from the ground state with orbital degeneracy of $J = 8$ state at Ho$^{3+}$ site with $C_{4h}$ point group symmetry.

The quadrupole-strain interaction for an ion, $\mathcal{H}_{QS} = -g \mu Q_{x} \alpha \varepsilon_{\alpha \beta}$, is a perturbation Hamiltonian for the ultrasonic measurements. Here the quadrupole moments $Q_{yz}$, $Q_{zx}$ with $E$-symmetry are responsible for $C_{44}$, $O_{2}'$ with $B$-symmetry for $(C_{11} - C_{12})/2$ and $O_{xy}$ with $B$-symmetry for $C_{66}$. A model consisting of $E$-doublet and $A$- or $B$-singlet at low excited energy $\Delta \sim 5$ K describes successfully the softening of the shear modes in HoB$_2$C$_2$ in terms of the quadrupole susceptibility. The solid line in Fig. 1 is a fit by a formula $C_{44} = C_{44}^{0}(T - T_{C}^{0})/(T - \Theta)$ with $T_{C}^{0} = 1.78$ K and $\Theta = 1.13$ K.
Inset of Fig. 1 shows a detail of the softening in $C_{44}$ and attenuation coefficient $\alpha_{44}$ over the successive phase transitions I-IV-III at low temperatures. It is remarkable that the softening of $C_{44}$ and attenuation $\alpha_{44}$ enhanced very much in phase IV between $T_{c1} = 5.9$ K and $T_{c2} = 5.0$ K. Employing the Debye-type dispersion of the attenuation coefficient, $\alpha(\omega) = (C_{\infty} - C_0)/2\rho v^3 \omega^2 \tau/(1 + \omega^2 \tau^2)$, we obtain a very slow relaxation rate $\tau = 7 \times 10^{-9}$ sec in phase IV. Other shear $(C_{11} - C_{12})/2$ and $C_{44}$ modes also show increase in attenuation coefficient in phase IV. This result means that the quadrupole moments coupled with the elastic strain of the ultrasound show a very slow fluctuation in phase IV, which is definitely distinguished from the behavior in the AFM phase III and the AFQ II in HoB$_2$C$_2$. The characteristic feature with fluctuation in both magnetic and quadrupole moments in phase IV suggests the order parameter of the higher order rank, presumably the octupole ordering.

The transverse $C_{44}$ mode of DyB$_2$C$_2$ in Fig. 2 reveals a softening of about 4\% below about 150 K down to $T_Q = 25$ K. Inset of Fig. 2 shows the successive transition from AFQ phase II to the AFM phase III. The transverse $(C_{11} - C_{12})/2$ mode of DyB$_2$C$_2$ shows also softening of 1.7\% in paramagnetic phase I, while the $C_{66}$ shows a monotonous increase above $T_Q$. In the tetragonal site-symmetry $C_{44}$, $J = 15/2$ splits into two kinds of Kramers doublets $E_{1/2}$ and $E_{3/2}$. The elastic softening in Fig. 2 is referred...
from an accidental degeneracy of Kramers doublets $E_{1/2}$ and $E_{3/2}$ for the ground state Dy$^{3+}$ at $C_{4h}$ site in DyB$_2$C$_2$. The solid line in Fig. 2 is a fit by $C_{44} = C_{44}^0 (T - T_Q)/(T - \Theta)$ with $T_Q^0 = 3.43$ K and $\Theta = 2.29$ K.

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\begin{align*}
\text{Fig. 2. Temperature dependence of } C_{44} \text{ of DyB}_2\text{C}_2. \text{ Inset shows the transition from paramagnetic phase I to AFQ phase II at } T_Q = 24.7 \text{ K and successive transition into AFM phase III at } T_N = 15.3 \text{ K.}
\end{align*}
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In summary the tetragonal compounds HoB$_2$C$_2$ and DyB$_2$C$_2$ in the present experiment show the elastic softening indicating the orbital degeneracy for the ground state of the 4f-systems. Considerable softening in the transverse $C_{44}$ mode in both compounds suggests that the quadrupole moments $O_{yz}$, $O_{zx}$ with $E$-symmetry are the most provable candidate for the order parameter in the AFQ phase. The ultrasonic attenuation in phase IV of HoB$_2$C$_2$ shows slow fluctuation rate of the quadrupole moment. Further experiment is required to establish the order parameter of the phase IV in HoB$_2$C$_2$.

REFERENCES