ULTRASONIC INVESTIGATION OF ANTIFERROQUADRUPOLE ORDERINGS IN HoB_2C_2 AND DyB_2C_2*

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(Received July 10, 2002)

The antiferroquadrupole orderings of the ternary rare earth compounds HoB_2C_2 and DyB_2C_2 have been investigated by means of ultrasonic measurements. The transverse $(C_{11} - C_{12})/2$, C_{44}, C_{66} modes in HoB_2C_2 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 HoB_2C_2 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 DyB_2C_2 above $T_Q = 24.7$ K indicates accidentally degenerated Kramers doublets of $E_{1/2}$ and $E_{3/2}$ for the ground state.

PACS numbers: 71.27.+a, 74.50.+r

The orbital as well as spin degrees of freedom in localized $4f$-electron system of rare earth compounds give rise to competitive inter-site interaction between the electric quadrupole moment and magnetic dipole moment. The $4f$-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 CeB_6 with Γ_8 ground state in a cubic lattice shows antiferroquadrupole (AFQ) ordering of O_{yz}, O_{zx} and O_{xy}

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

[1]. Yamaguchi *et al.* have reported that DyB_2C_2 with a tetragonal LaB_2C_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 λ-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_2C_2 [4]. Onodera *et al.* have recently found that the isomorphous compound HoB_2C_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_2C_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_2C_2 is distinguished from the appreciable magnetic Bragg peaks in phase III. In the present paper, we show ultrasonic investigation on HoB_2C_2 and DyB_2C_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_2C_2 and $\rho = 6.82 \times 10^2$ g/m^3 for DyB_2C_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_2C_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, $\mathcal{H}_{QS} = -g_\Gamma O_{\Gamma\gamma}\varepsilon_{\Gamma\gamma}$, is a perturbation Hamiltonian for the ultrasonic measurements. Here the quadrupole moments O_{yz}, O_{zx} with E-symmetry are responsible for C_{44}, O_2^2 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_2C_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.

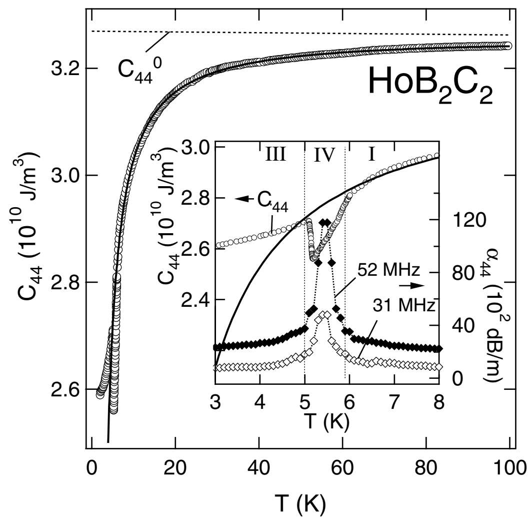

Fig. 1. Temperature dependence of C_{44} in HoB_2C_2 with a tetragonal structure. The solid line is a theoretical fit. Inset shows ultrasonic attenuation α_{44} and C_{44} around transition from paramagnetic phase I to ordered phase IV at $T_{c1} = 5.9$ K and successive transition to AFM phase III at $T_{c2} = 5.0$ K.

Inset of Fig. 1 shows a detail of the softening in C_{44} and attenuation coefficient α_{44} over the successive phase transitions I-IV-III at low temperatures. It is remarkable that the softening of C_{44} and attenuation α_{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_2C_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_2C_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_2C_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_{4h}, $J = 15/2$ 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_2C_2. The solid line in Fig. 2 is a fit by $C_{44} = C_{44}^0(T - T_c^0)/(T - \Theta)$ with $T_c^0 = 3.43$ K and $\Theta = 2.29$ K.

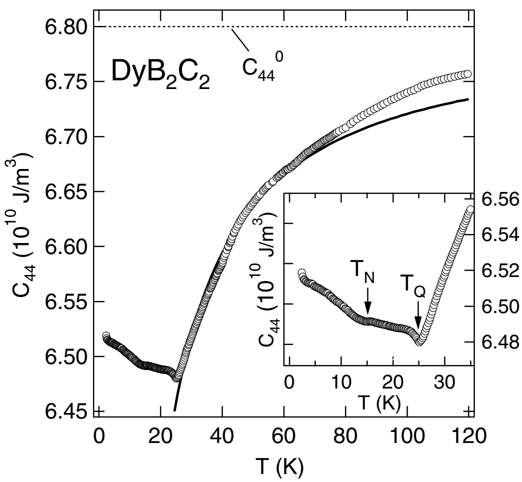

Fig. 2. Temperature dependence of C_{44} of DyB_2C_2. Inset shows the transition from paramagnetic phase I to AFQ phase II at $T_Q = 24.7$ K and successive transition into AFM phase III at $T_N = 15.3$ K.

In summary the tetragonal compounds HoB_2C_2 and DyB_2C_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_2C_2 shows slow fluctuation rate of the quadrupole moment. Further experiment is required to establish the order parameter of the phase IV in HoB_2C_2.

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