Quadrupolar Effect in Strongly Correlated Systems

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We have performed the ultrasonic measurement on the Kondo compound $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ and the charge fluctuation compound Yb_4As_3 to examine the quadrupolar effect. The magnetic phase diagram of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ is discussed in connection with the competition of the intersite interactions of the quadrupolar and magnetic moments to the Kondo coupling. The elastic softening of the C_{44} mode associated with the charge ordering in Yb_4As_3 is explained in terms of the susceptibility for the charge fluctuation mode with Γ_5 symmetry. [elastic constant, quadrupolar moment, Kondo effect, $\text{Ce}_x\text{La}_{1-x}\text{B}_6$, charge order, Yb_4As_3]

1. Introduction

Measurement of the elastic constant and the attenuation of the ultrasonic wave is a powerful method to examine the Kondo effect and the valence fluctuation phenomena in rare earth compounds. The 4f-state in rare earth ions with stable valency has the orbital freedom in addition to the spin freedom. The ground state multiplet due to the spin-orbit interaction splits into the crystalline electric field (CEF) state by the multipolar Coulomb potential in crystal. The magnetic moments described by the angular momentum J_x, J_y, J_z of the 4f-state lead the magnetic order or the Kondo effect at low temperatures. Furthermore, the quadrupolar moments described by the operator equivalent of O_{Γ_3} $\{O_2^0 = (2J_z^2 - J_x^2 - J_y^2)/\sqrt{3}, O_2^2 = J_x^2 - J_y^2\}$ and O_{Γ_5} $\{O_{yz} = J_y J_z + J_z J_y, O_{zx} = J_z J_x + J_x J_z, O_{xy} = J_x J_y + J_y J_x\}$ are relevant in rare earth compounds, because the orbital motion of the 4f-electron in the CEF potential makes the quadrupolar Coulomb field in the lowest order. The magnetic susceptibility is a probe to examine the response of the magnetic moment, while the elastic constant as a function of temperature is explained in terms of the quadrupolar response for the 4f-state. The quadrupole-strain interaction is the most important mechanism to reveal various elastic anomalies in the compounds containing the electronic states with the orbital freedom like 4f-orbit in rare earth, 3d-orbit in transition metal and the Landau orbit of conduction electrons in magnetic fields.

The charge fluctuation mode in the valence fluctuation compounds of rare earth systems may couple with the elastic strain of the ultrasonic wave. In the case of Yb_4As_3 presented in this paper, the transverse C_{44} mode exhibits characteristic softening above the structural phase transition point associated with the charge order. It

is an interested subject to elucidate the interplay of the charge freedom in the lattice system to the exotic magnetism like the heavy-Fermion properties in extremely low carrier system of Yb_4As_3 .

In the present paper we show the recent results of the ultrasonic investigation on the Kondo system of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ and the charge fluctuation compound of Yb_4As_3 . The quadrupolar effects in connection with orbital freedom as well as the charge freedom are emphasized.

2. $\text{Ce}_x\text{La}_{1-x}\text{B}_6$

The temperature dependence of $-\log T$ in the resistivity in the paramagnetic phase I of CeB_6 is an evidence of the Kondo scattering in the system [1]. At low temperatures, CeB_6 exhibits the phase transition into the antiferroquadrupolar phase II at $T_0 = 3.2\text{K}$ and the antiferromagnetic phase III appears successively below $T_N = 2.3\text{K}$ [2]. These long range orders in CeB_6 are dominated by the intersite interaction of the magnetic and quadrupolar moments associated with the Γ_8 ground state. In Fig. 1 we show the magnetic phase diagram which was determined by the ultrasonic measurement [3]. The increase of the phase boundary of I-II transition with increasing magnetic field indicates a peculiar stability of the phase II. The transition between the sub-phases II_A and II_B at relatively small critical field of 0.1T in Fig. 1 may be originated by the order parameter reorientation. The disagreement of the results of the neutron diffraction and NMR measurements was a long standing puzzle for the character of the order parameter in the phase II of CeB_6 [2, 4]. Quite recently Sakai et al. have proposed a model, where the antiferroquadrupolar order of O_{yz}, O_{zx}, O_{xy} -type characterized by the wave vector $\mathbf{k} = [1/2, 1/2, 1/2]$ is realized in the phase II of CeB_6 [5]. This model is

able to solve the contradiction between the neutron and NMR measurements. This model is also consistent with that the antiferroquadrupolar interaction $g'_{r5} = -2\text{K}$ for the moments of O_{yz} , O_{zx} , O_{xy} associated with the C_{44} mode is dominant in comparing with $g'_{r3} = -0.5\text{K}$ for $(C_{11}-C_{12})/2$ mode [6].

Fig. 1. Magnetic phase diagram of CeB_6 .

It is expected that the decrease of the cerium concentration in $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ may modify the magnetic phase diagram. The increase in the lattice constant from $a=4.140\text{ \AA}$ of CeB_6 to $a=4.156\text{ \AA}$ of LaB_6 means that the decreasing of the cerium concentration x introduces the negative chemical pressure in addition to the random dilution effect of the magnetic cerium ions by the non-magnetic lanthanum ions. In Fig. 2, we show the magnetic phase diagram of $\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6$ under magnetic field along [001] obtained by the ultrasonic measurement. As is shown in Fig. 3, the transverse C_{44} mode of $\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6$ exhibits a huge softening of 30% below $T_N=1.6\text{K}$, and increases abruptly below $T_Q=1.1\text{K}$. The inset of Fig. 3 shows that the softening of C_{44} at low temperatures in $\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6$ is suppressed considerably in applying the magnetic field. This softening of C_{44} disappears completely in the field above 1T. In the magnetic phase diagram of Fig. 2 we have introduced a new phase IV, which is not observed in the diagram of CeB_6 . Although the character of the phase IV in Fig. 2 is not clear at present stage, one may conclude that only the antiferromagnetic order is realized below $T_N=1.6\text{K}$, but the quadrupolar freedom is still relevant above $T_Q=1.1\text{K}$. The softening of the C_{44} mode below $T_N=1.6\text{K}$ means that the enhancement of the quadrupolar fluctuations of O_{yz} , O_{zx} , O_{xy} -type is induced in the phase IV. In comparing the

magnetic phase diagrams of CeB_6 and $\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6$, the antiferroquadrupolar transition T_Q of the I-II phase boundary is reduced much faster than the antiferromagnetic transition T_N with decreasing the cerium concentration x .

There is one more important energy scale of the Kondo temperature T_K , which means the energy gain in the formation of the Kondo singlet ground state below the excited state with mostly Γ_8 character in the present $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ system. Various experiments reveal that the Kondo temperature $T_K=1\text{K}$ of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ does not depend on the cerium concentration x [1, 7]. It is expected, therefore, that the crossover from the long range orders of the magnetic and/or quadrupolar moment to the non-magnetic ground state due to the one-site Kondo effect reveals in more diluted compounds with $x < 0.75$. We have performed already the ultrasonic experiments on the diluted compounds of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ with $x=0.7, 0.6, 0.5$. In the case of $x=0.7$, the antiferromagnetic order, probably the phase IV, is realized in zero magnetic field, but the antiferroquadrupolar order is found only in applied magnetic field.

Fig. 2. Magnetic phase diagram of $\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6$.

Next we discuss the magnetic phase diagram of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ in Fig. 4, where the non-magnetic ground state due to the Kondo effect is realized in zero magnetic field far below the Kondo temperature $T_K=1\text{K}$. The ordered phase II or III is stabilized only in the magnetic field above the critical field of $H_c=1.7\text{T}$. It should be noted that the phase III of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ is stable only in narrow field angle around [001], but the magnetic fields along [101] and [111] directions stabilize only the phase II. It is worth while to point out that the critical field $H_c=1.7\text{T}$ in Fig. 4 is a measure of the Kondo temperature $T_K=1\text{K}$ of the present system.

Fig. 3. Temperature dependence of the elastic constant C_{44} in $\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6$.

Fig. 4. Magnetic phase diagram of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$.

As shown in Fig. 5(a), the transverse C_{44} mode exhibits a marked softening of about 5% below 1 K down to a minimum point at 0.25 K [6]. The attenuation coefficient of the C_{44} mode in Fig. 5 (b) increases up to about 70 dB/cm in the ultrasound frequency 70 MHz below 1 K and dies out rapidly in lowering temperature below 0.4 K [8]. The peak height of the attenuation around 0.4 K obeys mostly the ω^2 -dependence. These large softening and attenuation in the C_{44} mode are originated from a huge fluctuation of the quadrupolar monuments O_{yz} , O_{zx} , O_{xy} -type for the excited state with Γ_8 character. In low temperatures below $T_K=1$ K, electrons fall into the Kondo singlet state, therefore, the elastic softening of C_{44} turns to minimum and its attenuation dies out simultaneously. In Figs. 6 (a) and (b), we show the low temperature behavior of the elastic constant C_{44} and its ultrasonic attenuation of

$\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ with increasing the magnetic field along [001]. C_{44} in the non-magnetic phase I of 30 mK and 330 mK increases abruptly at the I-III transition field of $H_C=1.7$ T, and shows small dip at the III-II transition point. The huge attenuation of the C_{44} mode at zero magnetic field decreases considerably with increasing the magnetic field up to $H_C=1.7$ T. In the phase III and II above $H_C=1.7$ T, the anomalous attenuation of the C_{44} mode dies out completely. These results in magnetic fields of Figs. 6 (a) and (b) indicate that the fluctuation of the quadrupolar moment in the non-magnetic state of the phase I is suppressed considerably in the magnetic fields. The critical magnetic field $H_C=1.7$ T is enough Zeeman energy to cause transition from the Kondo singlet ground state to the conventional ground state of Γ_8 .

Fig. 5 (a). Temperature dependence of the elastic constant C_{44} of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$.

Fig. 5 (b). Low temperature behavior of the ultrasonic attenuation of the transverse C_{44} mode in $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$.

Fig. 6 (a). Magnetic field dependence of C_{44} in $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ at low temperatures.

Fig. 6 (b). Magnetic field dependence of the ultrasonic attenuation of the transverse C_{44} mode in $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$.

The longitudinal C_{11} mode relating to the volume strain ϵ_B of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ shows the characteristic behavior under magnetic field in Fig. 7 (a). At the temperature of 1.45 K above the Kondo temperature $T_K=1\text{ K}$, the breakpoint associated with the phase transition from I to II is found. At lower temperature of 0.55 K below $T_K=1\text{ K}$, C_{11} shows a sharp drop at 1.85 T of the transition from I to III and breaks at about 4.0 T corresponding the transition from III to II. The ultrasonic attenuation of the longitudinal C_{11} mode in Fig. 7 (b) reveals the sharp peaks at the transition from the non-magnetic state of the phase I to the ordered phase III. The transverse C_{44} mode associated with the symmetry breaking strain ϵ_{F5} shows the huge softening as well as large attenuation in the non-magnetic state below $T_K=1\text{ K}$. The C_{11} mode with the volume strain ϵ_B , however, shows the anomaly only near the transition point from the phase I to III. This remarkable difference between the C_{11} and C_{44} modes with different symmetries relates to the characteristic feature of the quadrupole fluctuation in the system consisting of the Kondo singlet and the excited state with Γ_8 character.

Fig. 7 (a). Magnetic field dependence of elastic constant C_{11} in $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$.

Fig. 7 (b). Magnetic field dependence of ultrasonic attenuation of the longitudinal C_{11} mode in $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$.

The low temperature specific heat of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ in Fig. 8 is also important to characterize the non-magnetic state below $T_K=1\text{ K}$ [9]. The broad peaks around 0.8 K, which is dominated by the Kondo effect of the system, have been found in zero magnetic fields and $H=1.5\text{ T}$ in the non-magnetic state of the phase I. Above the critical magnetic field of $H_C=1.7\text{ T}$, appreciable peaks associated to the long range orders are observed. The peak A of $H=2.0\text{ T}$ in Fig. 8 corresponds to the phase transition from I to III, while the peaks C and B of 2.5 T mean the successive transitions of I-II-III. The considerably large peak D with a λ -type in higher magnetic field of $H=5.0\text{ T}$ corresponding to the I-II transition resembles to the result of I-II transition in CeB_6 . The specific heat coefficient $C/T=1.8\text{ J/mol K}^2$ in zero magnetic field of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ seems to be considerably large in comparing the results of $C/T=0.25\text{ J/mol K}^2$ in CeB_6 and $C/T=0.3\sim 0.4\text{ J/mol K}^2$ in $\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6$. This results of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ favors the scenario for the non-magnetic state due to the Kondo effect below $T_K=1\text{ K}$.

Fig. 8. Low temperature specific heat of $\text{Ce}_{0.5}\text{La}_{0.5}\text{B}_6$ in applied magnetic field along [001].

3. Yb_4As_3

Yb_4As_3 with the anti- Th_3P_4 structure of T_d^6 space group symmetry is characterized by valence fluctuation system consisting of Yb^{2+} and Yb^{3+} ions in the ratio of 3:1. At $T_c=292\text{K}$, the cubic phase of Yb_4As_3 changes into the trigonal structure of C_{3v}^6 , where one of the four body-diagonals of $\langle 111 \rangle$ direction shrinks slightly to be the angle $\alpha=90.8$ degree [10]. Recent neutron experiment in magnetic fields by Kohgi et al. showed that about 70% of Yb^{3+} ions with the magnetic moment of $J=7/2$ are ordered to be a short linear chain along $\langle 111 \rangle$ direction [11]. In spite of extremely low carrier, one part of 10^3 Yb ion, Yb_4As_3 exhibits the heavy-Fermion properties with the large specific heat coefficient $C/T=200\text{mJ/molK}^2$ and large T^2 -coefficient of the resistivity at low temperatures. These anomalies are discussed in connection with the low energy magnetic excitation of the linear chain of Yb^{3+} ions [12, 13], which is actually observed as one dimensional magnetic excitation by the neutron experiments [11].

We have performed the ultrasonic experiment to examine the interplay of charge freedom due to valence

fluctuation in Yb_4As_3 to its magnetic properties like heavy-Fermion compounds [14]. As is shown in Fig. 9, the C_{44} mode associated with the elastic strain ϵ_{yz} , ϵ_{zx} , ϵ_{xy} exhibits a remarkable softening of about 20% from 400K down to the structural transition point $T_c=292\text{K}$. Other transverse $(C_{11}-C_{12})/2$ mode and the longitudinal C_{11} mode show only step-like anomalies. The bulk modulus $C_B=(C_{11}+2C_{12})/3$ associated with the volume strain $\epsilon_B=\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}$ also shows only the step-like anomaly, but does not show softening. In the frame work of the Landau phenomenological theory, one can introduce the coupling term of the elastic strain ϵ_{yz} , ϵ_{zx} , ϵ_{xy} of the C_{44} mode to the charge fluctuation modes Q_{yz} , Q_{zx} , Q_{xy} of Yb^{2+} and Yb^{3+} ions in the system. This coupling leads the softening of $C_{44}=C_{44}^0(T-T_c^0)/(T-\theta)$, which can explain the result of Fig. 9 with the parameters $C_{44}^0=22.3\text{GPa}$, $T_c^0=247\text{K}$, $\theta=234\text{K}$.

Fig. 9. Temperature dependence of the elastic constants C_{11} , $(C_{11}-C_{12})/2$, C_B , C_{44} of Yb_4As_3 .

The first order nature of the transition, which is consistent that the phase transition point $T_c=292\text{K}$ is considerably higher than $T_c^0=247\text{K}$, is originated from the cubic invariant term of the third order for lack of inversion symmetry in the present crystal T_d^6 . The present analysis indicates that the charge fluctuation modes of Q_{yz} , Q_{zx} , Q_{xy} with Γ_5 symmetry quench at $T_c=292\text{K}$. Consequently the order parameter

$Q_{\Gamma_5}(111) = (\langle Q_{xy} \rangle + \langle Q_{zx} \rangle + \langle Q_{yz} \rangle) / \sqrt{3}$ below $T_c = 292\text{K}$ leads to the shrink of the lattice along $\langle 111 \rangle$ direction. It should be noted that the charge fluctuation mode of $Q_{\Gamma_5}(111)$ does not reproduce the "perfect order" of Yb^{3+} ions along $\langle 111 \rangle$ direction. Actually the neutron experiment showed that 70% of Yb^{3+} ions locate in the short chain along $\langle 111 \rangle$ direction.

No sign of the softening in the bulk modulus of Yb_4As_3 around $T_c = 292\text{K}$ means the ratio of Yb^{2+} and Yb^{3+} ions is conserved to be 3:1 in the charge order. The shallow minimum of C_{11} , $(C_{11} - C_{12})/2$ and C_{44} at around 40K in Fig. 9 means the coupling of the elastic strain to the magnetic excitation of Yb^{3+} ion in the linear short chain with low energy scale of $T^* \approx 40\text{K}$. The present measurement of the elastic softening showed the instability of the charge fluctuation mode with Γ_5 symmetry in Yb_4As_3 . The systematic investigation of the quadrupolar susceptibility for the charge fluctuation modes in the alloy compounds $\text{Yb}_4(\text{As}_{1-x}\text{Sb}_x)_3$ is also an interesting subject to elucidate the effect of the carrier doping to the system. These experiments are now in progress.

4. Conclusion

In this paper we have presented the elastic properties of the Kondo compounds $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ and the valence fluctuation compound Yb_4As_3 . In the case of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$, the quadrupolar moment of Γ_5 symmetry associated with the orbital freedom of the Γ_8 ground state is responsible for the elastic anomalies of C_{44} at low temperatures. The competition of the intersite interactions of the localized 4f-state to the Kondo coupling strongly modifies the magnetic phase diagram of the $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ system and provides the interesting phenomena connecting to the huge fluctuation of the quadrupolar moments with Γ_5 symmetry.

The charge fluctuation mode in Yb_4As_3 coupled with the elastic strain with Γ_5 symmetry leads to the softening of the transverse C_{44} mode above the charge ordering at $T_c = 292\text{K}$. The ordering of the charge freedom coupled with lattice distortion in low carrier system of Yb_4As_3 is a main issue to understand the exotic magnetism similar to the heavy-Fermion compound. The ultrasonic experiment focusing on the orbital and charge freedoms in strongly correlated systems is still important and stimulated subject.

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