Ferroquadrupole ordering and $\Gamma_5$ rattling motion in clathrate compound Ce$_3$Pd$_{20}$Ge$_6$

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Lattice effects in a cerium based clathrate compound Ce$_3$Pd$_{20}$Ge$_6$ with a cubic Cr$_{23}$C$_6$-type structure have been investigated by ultrasonic and thermal expansion measurements. Elastic softening of $(C_{11} - C_{12})/2$ and $C_{44}$ proportional to the reciprocal temperature $1/T$ above $T_{Q1} = 1.25$ K are well described in terms of the quadrupole susceptibility for the ground state $\Gamma_8$. A huge softening of 50% in $(C_{11} - C_{12})/2$ and a spontaneous expansion $\Delta L/L = 1.9 \times 10^{-4}$ along the [001] direction in particular indicate the ferroquadrupole ordering of $O_2$ below $T_{Q1}$. The elastic anomalies associated with the antiferromagnetic ordering at $T_{N2} = 0.75$ K and the incommensurate antiferromagnetic ordering are also found. Notable frequency dependence of $\chi$ and $\omega^2$ along the [111] direction with eight fractionally occupied positions around the 4a site in a cage. The thermally activated $\Gamma_5$ rattling motion obeying a relaxation time $\tau = \tau_0 \exp(E/k_B T)$ with an attempt time $\tau_0 = 3.1 \times 10^{-11}$ sec and an activation energy $E = 70$ K dies out with decreasing temperature, and then the off-center tunneling state of Ce ion in the 4a-site cage will appear at low temperatures.

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I. INTRODUCTION

The 4f-electronic systems with spin and orbital degrees of freedom in rare earth compounds frequently reveal electric quadrupole orderings in addition to magnetic dipole orderings at low temperatures. The cubic compounds based on Ce$^{3+}$ ion with a $\Gamma_8$ quartet ground state in particular have received much attention because the competitive phenomena associated with magnetic dipole, electric quadrupole and magnetic octupole degrees of freedom are expected. The direct product of $\Gamma_8 \otimes \Gamma_8$ is reduced to a direct sum $\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus 2\Gamma_4 \oplus 2\Gamma_5$. The magnetic dipole $J_x, J_y, J_z$ belonging to $\Gamma_4$ symmetry are order parameters for magnetic orderings. The quadrupole orderings of $O_2^2, O_2^4$ with $\Gamma_3$ or $O_{yz}, O_{xz}, O_{xy}$ with $\Gamma_5$ are interesting phenomena in the $\Gamma_8$ system. We refer to CeAg exhibiting the ferroquadrupole (FQ) ordering of $O_2^2$ at $T_{Q} = 15$ K.$^{1,2}$ CeB$_6$ is known as the antiferroquadrupole (AFQ) ordering of $O_{xy}$-type with the propagation vector of $k = [111]$ at $T_{Q} = 3.2$ K.$^{3,4}$ The octupole moments $T_{xyz}$ with $\Gamma_2$ symmetry, $T_x^3, T_y^3, T_z^3$ with $\Gamma_4$ and $T_x^\beta, T_y^\beta, T_z^\beta$ with $\Gamma_5$ may play a role in the $\Gamma_8$ system.$^{5}$

A cerium-based ternary compound Ce$_3$Pd$_{20}$Ge$_6$ with the $\Gamma_8$ ground state has received much attention because the competition between quadrupole and magnetic orderings is expected at low temperatures.$^{6}$ Ce$_3$Pd$_{20}$Ge$_6$ crystallizes in a cubic Cr$_{23}$C$_6$-type structure with a space group $Fm\overline{3}m$ consisting of four molecular units with 116 atoms in a unit cell.$^{7}$ The twelve Ce sites located in cages are divided into two nonequivalent sites in crystallography. As shown in Fig. 1 the Ce ion at 4a site in a cage consisting of twelve Pd-atoms and six Ge atoms possesses point group symmetry O$_b$, while the Ce ion at 8c site in a cage of sixteen Pd atoms has T$_d$. The 4a sites form a face-centered cubic lattice, while the 8c sites make a simple cubic lattice. Inelastic neutron scattering on Ce$_3$Pd$_{20}$Ge$_6$ revealed overlapping two peaks for the crystalline electric field (CEF) potentials, which correspond to magnetic dipole transitions from the $\Gamma_8$ ground quartet to the $\Gamma_7$ excited doublet at 60 K of the 4a site and from the $\Gamma_8$ ground quartet to the $\Gamma_7$ at 46 K of 8c site.$^{8}$ The entropy obtained by low-temperature specific heat measurement on Ce$_3$Pd$_{20}$Ge$_6$ also indicates the ground state $\Gamma_8$ quartet at both 4a and 8c sites.$^{9}$

The low-temperature specific heat of Ce$_3$Pd$_{20}$Ge$_6$ shows a rounded small peak at $T_{Q1} = 1.25$ K and a sharp $\lambda$-peak at $T_{N2} = 0.75$ K.$^{9}$ Magnetic susceptibility shows a clear cusp at $T_{N2}$, but exhibits no sign of anomaly at $T_{Q1}$.$^{9}$ In addition to these experimental results, an elas-
elasticty is favorable for application to thermoelectric device because their remarkable reduction of thermal conductivity or off-center motion in a cage have received attention. The ferroquadrupole ordering below $T_{Q_1}$ is relevant for the 8c sites and the antiferromagnetic ordering below $T_{N_2}$ occurs at 4a sites. The $\Gamma_5$ rattling motion originates from the off-center Ce1 atom in 4a-site cage.

The clathrate compounds exhibiting the rattling motion or off-center motion in a cage have received attention because their remarkable reduction of thermal conductivity is favorable for application to thermoelectric device with a high figure of merit. The ultrasonic waves are scattered by the rattling motion in an over-sized cage of a semiconductor Sr$_8$Ge$_{16}$Se$_{30}$ and a filled skutterudite compound PrOs$_4$Sb$_{12}$. The off-center tunneling motion of OH ion doped in NaCl gives rise to elastic softening at low temperatures. The rattling motion in the present compound Ce$_3$Pd$_{20}$Ge$_6$ with clathrate structure has not been reported so far.

In the present paper we show ultrasonic measurements on Ce$_3$Pd$_{20}$Ge$_6$ in order to examine lattice effects associated with the quadrupole ordering and rattling motion in the system. The thermal expansion measurement is also employed to detect the spontaneous distortion below $T_{Q_1}$. In Sec. II, the experimental procedure and apparatus are described. The results of the elastic constant, magnetic phase diagram, thermal expansion are presented in Sec. III. The ultrasonic dispersion due to rattling motion is also argued in Sec. II. In Sec. IV, we present concluding remarks.

II. EXPERIMENT

Single crystals of Ce$_3$Pd$_{20}$Ge$_6$ used in the present measurements were grown by a Czochralski pulling method. We have made the ultrasonic velocity measurements using an apparatus consisting of a phase difference detector. Piezoelectric plates of LiNbO$_3$ for the ultrasonic wave generation and detection are bonded on plane parallel surfaces of sample. The $x$-cut plate of LiNbO$_3$ is available for transverse ultrasonic waves and the 36°$y$-cut plate is for longitudinal waves. The ultrasonic velocity $v$ was measured by fundamental frequencies of 10 MHz and overtone excitations of 30, 50 and 70 MHz. In the estimation of the elastic constant $C = pv^2$, we use the mass density $\rho = 10.254$ g/cm$^3$ for Ce$_3$Pd$_{20}$Ge$_6$ with a lattice parameter $a = 12.457$ Å.

A homemade $^3$He-refrigerator equipped with a superconducting magnet was used for low-temperature measurements down to 450 mK in magnetic fields up to 12 T. A $^3$He-$^4$He dilution refrigerator with a top-loading probe was used for the ultrasonic measurements in low-temperature region down to 20 mK in fields up to 16 T. Low input-power condition provides the low-temperature ultrasonic measurements free from a self-heating effect in the ultrasonic transducers. The sample length as a function of temperature or applied magnetic field was measured precisely by a capacitance dilatometer in the $^3$He-refrigerator.

III. RESULTS AND DISCUSSIONS

A. Temperature dependence of the elastic constants

The elastic constants of $C_{11}$ and $C_L = (C_{11} + C_{12} + 2C_{44})/2$ of Ce$_3$Pd$_{20}$Ge$_6$ in Fig. 2 were measured by the longitudinal ultrasonic waves with frequencies 10 MHz propagating along the [100] and [110] directions, respectively. The elastic constant $(C_{11} - C_{12})/2$ of Ce$_3$Pd$_{20}$Ge$_6$ in Fig. 3 was measured by the transverse ultrasonic wave of 10 MHz propagating along the [100] direction polarized to the [110] one. The elastic constant $C_{44}$ of Ce$_3$Pd$_{20}$Ge$_6$ in Fig. 3 was determined by the transverse wave of 30 MHz propagating along [100] polarized to [010]. The bulk modulus $C_B = (C_{11} + 2C_{12})/3$ in Fig. 2 was calculated by $C_{11}$ in Fig. 2 and $(C_{11} - C_{12})/2$ in Fig. 3.

It is remarkable that $(C_{11} - C_{12})/2$ exhibits a huge softening of 50% with decreasing temperature down to $T_{Q_1} = 1.25$ K. In phase II below $T_{Q_1}$ the ultrasonic echo
signal of the \((C_{11} - C_{12})/2\) mode completely disappears due to a marked ultrasonic attenuation. The softening of the longitudinal \(C_{11}\) and \(C_L\) modes in Fig. 2 originates from the softening of \((C_{11} - C_{12})/2\), because \(C_{11}\) and \(C_L\) involve \((C_{11} - C_{12})/2\) in part. The softening of \((C_{11} - C_{12})/2\) above \(T_{Q1}\) and the spontaneous tetragonal distortion below \(T_{Q1}\), that will be shown in Sec. III D, provide evidence for the FQ ordering in phase II. The \(C_{44}\) in Fig. 3 also exhibits a softening of 2.5% down to \(T_{Q1}\). The low-temperature behavior of \(C_{11}\) and \(C_{44}\) shown in insets of Figs. 2 and 3 indicates the transition to the FQ phase II at \(T_{Q1}\) and successive transition to the AFM phase III at \(T_{N2} = 0.75\) K. On the other hand, \(C_B\) shows monotonic increase with decreasing temperature.

Neutron scattering on Ce₃Pd₂₀Ge₆ revealed the paramagnetic state for Ce ions at both 4a and 8c sites in phase II, which is consistent with the present scenario of the FQ ordering at 8c site in phase II below \(T_{Q1}\). The AFM ordering in phase III at 4a site below \(T_{N2}\) has been detected by the neutron scattering. It has been proposed that the inter-site quadrupole interaction among 8c sites brings about the FQ ordering at 8c sites in phase II and Ce ions at 4a sites still remain to be the para-state even in phase II. The inter-site magnetic interaction among 4a sites gives rise to the AFM ordering in phase III below \(T_{N2}\). The magnetic ordering at 8c sites appears only below 0.4 K. We discuss about this transition in the following Sec. III C.

### B. Quadrupole susceptibility

In order to analyze the elastic softening of \((C_{11} - C_{12})/2\) and \(C_{44}\) in Ce₃Pd₂₀Ge₆ of Fig. 3, we introduce the coupling of the quadrupole \(O_{\Gamma\gamma}\) of Ce ions to the elastic strain \(\varepsilon_{\Gamma\gamma}\) as

\[
H_{QS} = - \sum_i g_{\Gamma}(i)\varepsilon_{\Gamma\gamma},
\]

where the summation \(\sum_i\) takes over Ce ions in unit volume and \(g_{\Gamma}\) is a coupling constant. The inter-site quadrupole interaction mediated by phonons and conduction electrons is written in a mean field approximation as

\[
H_{QQ} = - \sum_j g_{\Gamma}(j)\langle O_{\Gamma\gamma}\rangle O_{\Gamma\gamma}(j),
\]

where \(\langle O_{\Gamma\gamma}\rangle\) denotes a mean field of the quadrupole and \(g_{\Gamma}\) means a coupling constant for the inter-site quadrupole interaction. By differentiating the total free energy consisting of 4f-electron and lattice parts with respect to the elastic strain \(\varepsilon_{\Gamma\gamma}\), we obtain the temperature dependence of the elastic constant \(C_{\Gamma}(T)\) as

\[
C_{\Gamma}(T) = C_{\Gamma}^0 - \frac{Ng_{\Gamma}^2\chi_{\Gamma}(T)}{1 - g_{\Gamma}\chi_{\Gamma}(T)},
\]
Here \( C(T) \) denotes a background elastic constant without the quadrupole-strain interaction and \( N \) is the number of Ce ions in unit volume. The quadrupole susceptibility of \( \chi_T \) in Eq. (3) is written as

\[
-g^2\partial^2\chi_T(T) = \left( \frac{\partial^2 E_i}{\partial \varepsilon_{T\gamma}} \right) - \frac{1}{k_B T} \left( \left( \frac{\partial E_i}{\partial \varepsilon_{T\gamma}} \right)^2 - \left( \frac{\partial^2 E_i}{\partial \varepsilon_{T\gamma}^2} \right) \right) \]

where \( E_i \) is a second-order perturbation energy with respect to \( \varepsilon_{T\gamma} \) for CEF state. The first part in right hand side of Eq. (4) corresponds to the Van Vleck-term and the second part to the Curie term. The Ce ions at both 4a and 8c sites in Ce\(_3\)Pd\(_{20}\)Ge\(_6\) have the \( \Gamma_8 \) ground state, while the \( \Gamma_7 \) state has excited energies of 46 K at 8c site and 60 K at the 4a site. As was already mentioned, the neutron scattering revealed that the FQ ordering of 8c sites occurs at \( T_{Q1} = 1.25 \) K and the AFM ordering of 4a sites appears at \( T_{N2} = 0.75 \) K. These facts indicate that the inter-site quadrupole interaction of Eq. (2) among the Ce ions at 8c sites dominates the softening of \( (C_{11} - C_{12})/2 \) as a precursor of the FQ ordering at \( T_{Q1} \). In the following analysis we simply assume the quadrupole-strain interaction of Eq. (1) and quadrupole interaction of Eq. (2) for the 8c site with the CEF splitting of \( \Gamma_8 \) (0 K) and \( \Gamma_7 \) (46 K).

The solid lines for \( (C_{11} - C_{12})/2 \) and \( C_{44} \) with Eq. (3) in Fig. 3 reproduce well the softening in paramagnetic phase I above \( T_{Q1} \). It should be noted that the softening above \( T_{Q1} \) proportional to the reciprocal temperature \( 1/T \) originates from the Curie term of Eq. (4). The coupling constants were determined to be \( g_T^{13} = 107 \) K, \( g_T^{15} = 0.01 \) K for \( (C_{11} - C_{12})/2 \) and \( g_T^{15} = 89 \) K, \( g_T^{15} = 0.19 \) K for \( C_{44} \). The background \( (C_{11}^{0} - C_{12}^{0})/2 = (4.12 - 0.001T) \times 10^{10} \text{ J/m}^3 \) and \( C_{44}^{0} = (3.44 - 0.0007T) \times 10^{10} \text{ J/m}^3 \) indicated by broken lines in Fig. 3 was used. The positive value of \( g_T^{13} > 0 \) are consistent with the FQ ordering in Ce\(_3\)Pd\(_{20}\)Ge\(_6\). A shoulder like anomaly in \( C_{44} \) around 10 K results from ultrasonic dispersion that is caused by a rattling motion of the rare-earth ion at 4a site in an oversized cage of Fig. 1. We discuss about this remarkable behavior in Sec. III E.

### C. Magnetic phase diagram

In order to examine the magnetic phase diagrams of the FQ and AFM orderings in Ce\(_3\)Pd\(_{20}\)Ge\(_6\), we have made the low-temperature ultrasonic measurements of \( C_{11}, C_{44} \) and \( (C_{11} - C_{12})/2 \) under magnetic fields. The softening of \( C_{11} \) of Fig. 4 reduces with increasing fields applied along the [001] direction parallel to the propagation direction of longitudinal wave. The FQ transition points \( T_{Q1} \) indicated by downward arrows in Fig. 4 shift to higher temperatures and become indistinct in high fields up to 6 T. In Fig. 5, the FQ transition points \( T_{Q1} \) also shift to higher temperatures accompanied by reduction of the softening in \( C_{44} \) with increasing applied fields along the [001] direction.

In Figs. 6 and 7, we show the field dependence of \( (C_{11} - C_{12})/2 \) applying fields along the [001] and [110] directions, respectively. In zero magnetic field, the \( (C_{11} - C_{12})/2 \) mode exhibits the considerable softening of 50% and the strong ultrasonic attenuation losing the echo signal in the vicinity of the FQ transition \( T_{Q1} = 1.25 \) K. The magnitude of the softening decreases abruptly with increasing fields along both [001] and [110] directions.
served in high fields of 5 T. This behavior of T is only broad round anomalies around phase I to the FQ phase II shift to higher temperatures, T corresponding to the transitions C44 to the results of the FQ ordering accompanied by the soft magnetic fields. In Fig. 7 the anomalies associated with the shifts slightly to lower temperatures with increasing magnetic fields. In magnetic fields, clear minima of (C11 − C12)/2 of Ce3Pd20Ge6 under magnetic fields along the [001] direction. The successive phase transitions I-II-III are indicated by arrows.

In magnetic fields, clear minima of (C11 − C12)/2 corresponding to the transitions TQ1 from the paramagnetic phase I to the FQ phase II shift to higher temperatures. Only broad round anomalies around TQ1 have been observed in high fields of 5 T. This behavior of TQ1 is similar to the results of the FQ ordering accompanied by the soft C44 mode in HoB6.17 The Neel temperature TN2 in Fig. 6 shifts slightly to lower temperatures with increasing magnetic fields. In Fig. 7 the anomalies associated with the transition between phase II and II’ below TQ1 have been found.

For the investigation of low-temperature and high-field behavior in FQ II and AFM III phases, we have measured field dependence of the C44 and C1 = (C11 + C12 + 2C44)/2 employing the dilution refrigerator. In Fig. 8 we show C14 versus H at 30 mK in fields up to 12 T applied along [001]. Inset of Fig. 8 is expanded view below 2.5 T. An anomaly of the phase II-III boundary at 2.1 T indicated by a vertical line has been observed. Furthermore, several anomalies at 0.5, 1.2 and 1.6 T associated with sub-phases of the phase III have been found. It should be emphasized that appreciable hysteresis phenomena between increasing and decreasing field sequences have been found only in phase III.

In Fig. 9 we show the low-temperature field dependence of the C1 in fields up to 16 T applied along [110]. Low-field behavior below 2.5 T is shown in inset of Fig. 9. We have observed a new phase boundary around 8.2 T in phase II, which is probably a sub-phase of the FQ phase II. However, this phase boundary is absent in fields along [001] as shown in Fig. 8. At low field in phase III, we have found several anomalies in C1, of Fig. 9 showing a hysteresis behavior. As can been seen in inset of Fig. 9, this hysteresis becomes pronounced with decreasing temperature. These sub-phases with hysteresis behavior in phase III in magnetic fields along both [001] and [110] are well consistent with the results of neutron scattering experiments that detect weak incommensurate magnetic Bragg peaks with a propagation vector k = [0 0 1-τ], (τ ∼ 0.06) at 8c site.11

The magnetic phase diagrams of Ce3Pd20Ge6 in Figs. 10 and 11 are obtained in fields along the [001] and [110] directions, respectively. We present the results of the ultrasonic measurements together with the results of thermal expansions in Sec. III D. It is of importance that the FQ phase II is stabilized in fields for the [001] direction in Fig. 10 and the [110] direction in Fig. 11. The FQ sub-phase II’ was added to the phase diagram and the upper limit at 8.2 T of the phase II’ newly determined in fields along [110] of Fig. 11. However, the FQ sub-phase is absent in fields along [001] of Fig. 10. This result indicates strong anisotropy of the quadrupole interaction of O2 in Ce3Pd20Ge6.

The series of R2Pd20X6 compounds usually show two successive AFM orderings of 8c site at TN1 with a propagation vector k1 = [111] and of 4a site at TN2 (< TN1) with k2 = [001], Nd2Pd20Ge6 (TN1 = 1.75 K, TN2 = 0.58 K)18, Nd2Pd20Si6 (TN1 = 2.4 K, TN2 = 0.7 K)19, Tb2Pd20Si6 (TN1 = 10.2 K, TN2 = 4.1 K)20, Dy2Pd20Si6 (TN1 ∼ 5.8 K, TN2 ∼ 1.8 K)21 and so on. One can reasonably expect that the transition temperature TN1 at 8c site is always higher than TN2 at 4a site since the distance ∼ 6.2 Å between rare-earth ion of 8c site is much shorter than the one ∼ 8.8 Å of 4a site. In the present Ce3Pd20Ge6, at first the FQ ordering at 8c site with a structural change from cubic lattice to tetragonal one occurs at TQ1 = 1.25 K. Therefore, the AFM
ordering at 8c site is hard to take place because the favorable propagation vector $k_1 = [111]$ of 8c site does not match to the tetragonal lattice in phase II. In other words, the AFM ordering at 8c site is replaced by the FQ ordering in Ce$_3$Pd$_{20}$Ge$_6$. While, the AFM ordering of 4a site with a propagation vector $k_2 = [001]$ is easy to occur even in tetragonal structure below $T_{N2}$. Neutron experiments detected large enough value of saturation cerium moments $\mu(4a) = (1.1 \pm 0.1)\mu_B$/Ce that is expected from the ground state quartet $\Gamma_8$ perpendicular to the $k_1 = [001]$ in Ce$_3$Pd$_{20}$Ge$_6$ far below $T_{N2}$ at 50 mK.\textsuperscript{11}

FIG. 8: Field dependence of the $C_{44}$ at 30 mK in fields along [001] up to 12 T. Inset is expanded view below 2.5 T indicating the magnetic transitions.

FIG. 9: Field dependence of the $C_L = (C_{11} + C_{12} + 2C_{44})/2$ at various temperatures in fields along [110] up to 16 T. Inset is expanded view below 2.5 T indicating the magnetic transitions.

FIG. 10: Magnetic phase diagram of Ce$_3$Pd$_{20}$Ge$_6$ under fields along the [001] direction. The boundary from paramagnetic phase I to the ferroquadrupole phase II shifts to higher temperatures with increasing fields, while the boundary from phase II to the antiferromagnetic phase III shifts to lower temperatures in fields.

FIG. 11: Magnetic phase diagram of Ce$_3$Pd$_{20}$Ge$_6$ under fields along the [110] direction. The sub-phase II' exists in the AFQ phase II.
D. Thermal expansion

In order to examine the structural change due to the FQ ordering at $T_{Q1} = 1.25$ K, we have measured the thermal expansion along the [001] direction in Ce$_3$Pd$_{20}$Ge$_6$. The sample lengths along the [001] and [111] directions are written by the symmetry strains as $(\Delta L/L)_{[001]} = \varepsilon_{zz} = \varepsilon_B/3 + \varepsilon_u/\sqrt{3} + 2(\varepsilon_{yz} + \varepsilon_{zx} + \varepsilon_{xy})/3$. Here, $\varepsilon_B = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$ is a volume strain with $\Gamma_1$ symmetry, $\varepsilon_u = (2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})/\sqrt{3}$ is a tetragonal strain with $\Gamma_3$ and $\varepsilon_{xy}$ is a shear strain with $\Gamma_5$. The length along [001] in Fig. 12 shows a monotonous decrease with decreasing temperature in paramagnetic phase I above $T_{Q1}$ and abruptly expands about $\Delta L/L = 1.9 \times 10^{-4}$ below $T_{Q1}$. The thermal expansion along [001] in phase II and the huge softening of 50% in $(C_{11} - C_{12})/2$ of Fig. 3 indicate the $O_{h}^{4}$-type FQ ordering accompanied by the structural transition from cubic lattice to tetragonal one with the spontaneous strain $(\varepsilon_u)_{II}$ in phase II. This spontaneous strain is proportional to the order parameter as $(\varepsilon_u) = Nq_{34}(O_{h}^{4})/(2/(C_{11} - C_{12}))$ in mean-field approximation. Below $T_{N2} = 0.75$ K, the $\Delta L/L$ along [001] slightly shrinks. Inset of Fig. 12 is expanded view of $\Delta L/L$ and the coefficient of the thermal expansion $\alpha$ at low temperatures. A sharp anomaly in the coefficient $\alpha$ has been found at the FQ transition $T_{Q1}$.

Measurements of $\Delta L/L$ versus $T$ in various magnetic fields parallel to [001] are shown in Fig. 13. The magnitude of the expansion $\Delta L/L$ in fields exhibits noticeable increase up to $\Delta L/L = 2.5 \times 10^{-4}$ compared with that in zero magnetic field. The sharp increase of $\Delta L/L$ at the transition point to the FQ phase II has been observed in low magnetic fields below 1 T. On the other hand, the gradual increase in the thermal expansion $\Delta L/L$ above 5 T up to 12 T indicates an obscure character of the I-II phase boundary in high fields. This is consistent with the fact that the elastic constants in fields of Figs. 4, 5, 6 and 7 show obscure transitions in fields. This behavior is similar to the liquid-gas transition near the critical end point under hydrostatic pressures.

The thermal expansion along the [001] direction in fields parallel to [001] and the considerable softening of $(C_{11} - C_{12})/2$ of 50% in Ce$_3$Pd$_{20}$Ge$_6$ strongly suggests that the order parameter of the FQ ordering in phase II is $O_{h}^{4}$ with $\Gamma_3$ symmetry. The relatively small softening of 2.5% in $C_{44}$ in Fig. 3 means that the quadrupole of $O_{xy}$-type with $\Gamma_5$ is irrelevant for the transition at $T_{Q1}$. The thermal expansion of Ce$_3$Pd$_{20}$Ge$_6$ along [111] is required to examine an interplay of the spontaneous strain $\varepsilon_{xy}$ for the phase II. We refer to our recent study of the FQ transition in HoB$_6$ and the phase IV in Ce$_3$La$_{1-x}$B$_6$ ($x=0.75$, 0.70),\textsuperscript{17,22} where the trigonal strain $\varepsilon_{yz} = \varepsilon_{xx} = \varepsilon_{xy}$ plays a significant role and the tetragonal strain $\varepsilon_u$ is irrelevant. These facts are well consistent with the pronounced elastic softening in $C_{44}$ of 70% in HoB$_6$ and of 31% in Ce$_3$La$_{1-x}$B$_6$ ($x=0.75$, 0.70).

E. Ultrasonic dispersion of $C_{44}$

The $C_{44}$ mode associated with the elastic strain $\varepsilon_{yz}, \varepsilon_{xx}, \varepsilon_{xy}$ of $\Gamma_5$ symmetry of Ce$_3$Pd$_{20}$Ge$_6$ in Figs. 3 and 5 exhibits a shoulder like anomaly around 10 K in addition to the characteristic softening due to the quadrupole.
lar coupling above $T_{Q1} = 1.25$ K. It should be noted that this anomaly is absent for the $(C_{11} - C_{12})/2$ mode associated with $\Gamma_3$ elastic strain $\varepsilon_v$ and the bulk modulus $C_B$ with $\Gamma_1$ volume strain $\varepsilon_B$. In order to examine the origin of this anomaly, we have measured the frequency dependence of $C_{44}$ from 10 MHz up to 250 MHz. The elastic constant $C_{44}$ of Fig. 14(a) exhibits shoulders showing remarkable frequency dependence. An increase in ultrasonic attenuation around shoulder has also been found, but not discussed here. We describe this frequency dependence of the elastic constant $C_{44}^D(\omega)$ in terms of Debye-type dispersion as

$$C_{44}^D(\omega) = C_{44}^D(\infty) - \frac{C_{44}^D(0)}{1 + \omega^2 \tau^2}, \quad (5)$$

where $C_{44}^D(\infty)$ and $C_{44}^D(0)$ are the elastic constants of high frequency limit and low frequency one, respectively. Here $\omega$ is an angular frequency of the ultrasonic wave and $\tau$ means the relaxation time of the system. In fittings of Fig. 14(b), we take into account the superposition of two susceptibilities by the quadrupole one of Eq.(3) and the Debye-type dispersion of Eq.(5) as $C_{44} = C_{44}^Q + C_{44}^D(\omega)$. The inflection points around 10 K in $C_{44}$ indicated by arrows in Fig. 14(a) mean the temperatures where the $\tau$ coincides with the $\omega$ as $\omega\tau = 1$. The ultrasonic attenuation is expected to be maximum at the temperatures for $\omega\tau = 1$. The solid lines of Fig. 14(b) being the calculations with Eq. (5) well reproduce the experimental results of Fig. 14(a). The relaxation time obeying the Arrhenius-type temperature dependence $\tau = \tau_0 \exp(E/k_B T)$ with the attempt time $\tau_0 = 3.1 \times 10^{-11}$ sec and the activation energy $E = 70$ K has been determined. The parameter of $\Delta C = C_{44}^D(\infty) - C_{44}^D(0) = 0.004 \times 10^{10}$ J/m$^3$ is used.

The ultrasonic dispersion due to electron thermal hopping has already found in the inhomogeneous valence fluctuation compounds of Sm$_3$X$_4$ (X=Se, Te), Yb$_4$(As$_{0.71}$Sb$_{0.29}$)$_4$$_{23}$ and Sr$_{12}$Ca$_2$Cu$_{24}$O$_{41}$$_{24}$. It is remarkable that the very slow relaxation time $\tau$ and extremely low activation energy $E$ for Ce$_3$Pd$_{20}$Ge$_6$ are exceptional as compared to those of charge fluctuation compounds Sm$_3$Se$_4$$_{25}$ and Sm$_3$Te$_4$$_{26}$, $\tau_0 \sim 2.5 \times 10^{-13}$ sec and $E \sim 1600$ K, and Sr$_{12}$Ca$_2$Cu$_{24}$O$_{41}$, $\tau_0 \sim 1.01 \times 10^{-13}$ sec and $E \sim 1900$ K. This discrepancy of the order of $\tau_0$ and $E$ between the present Ce$_3$Pd$_{20}$Ge$_6$ and the charge fluctuation compounds indicates that thermally activated rattling motion of heavy mass particle, which is probably rare-earth ion in a cage, gives rise to the ultrasonic dispersion in Ce$_3$Pd$_{20}$Ge$_6$.

Glass materials and charge fluctuation compounds exhibit frequently the ultrasonic dispersion, which results from a thermally activated motion in a double- or multi-well potential. The compounds such as Sm$_3$X$_4$ (X=S, Se, Te) with different valence of Sm$^{2+}$ and Sm$^{3+}$ ions and Sr$_{12}$Ca$_2$Cu$_{24}$O$_{41}$ with Cu$^{2+}$ and Cu$^{3+}$ ions cause the ultrasonic dispersions due to thermally assisted charge fluctuation in the temperature region between 100-200 K. The two-level system (TLS) due to an atomic tunneling or electron tunneling manifests itself in glass materials at low temperatures, where the thermally activated motion dies out. The TLS yields the decrease in the elastic constant proportional to $\ln T$,$^{28}$ the specific heat to $T$ and thermal conductivity to $T^2$. Besides in the case of Sm$_3$Te$_4$, remarkable logarithmic decrease in the elastic constant appears below about 15 K down to the spin glass transition at $T_g = 1.5$ K, which suggests the existence of the 4f-electron tunneling motion between Sm$^{2+}$ and Sm$^{3+}$ ions situated charge glass state.$^{26}$

The present clathrate compound Ce$_3$Pd$_{20}$Ge$_6$ is a crystal possessing an ideal periodic arrangement of cages in space. The stable trivalent Ce ions in cages of Ce$_3$Pd$_{20}$Ge$_6$ are free from the valence fluctuation phenomena. As shown in Fig. 1, the clathrate compound Ce$_3$Pd$_{20}$Ge$_6$ is made up of the cage at 4a site consisting of Pd and Ge with distances $d_{Ce1-Ge6}=3.332$ Å, $d_{Ce1-Pd2}=3.067$ Å, and the cage at 8c site of Pd with $d_{Ce2-Pd1}=2.868$ Å, $d_{Ce2-Pd2}=3.373$ Å. The trivalent Ce ion with radii $a = 1.7 \sim 1.8$ Å inside the 4a-site cage in particular is expected to show the rattling motion over the off-center positions being away from the center of the cage. Actually the neutron scattering on Pr$_3$Pd$_{20}$Ge$_6$ and Nd$_3$Pd$_{20}$Ge$_6$ revealed the sharp transition peaks indicating the stable CEF splitting at 8c site and no indication for CEF state at 4a site.$^9$ These results may imply...
the obscure CEF state due to the off-center Ce ion at 4a site contrary to the well-defined CEF splitting at 8c site being stable Ce ion position.

**F. \( \Gamma_5 \) rattling motion**

Notable finding of Fig. 14 is that the ultrasonic dispersion in the \( C_{44} \) mode associated with \( \varepsilon_{xy} \)-type strain indicates the rattling motion with specific \( \Gamma_5 \) symmetry in Ce\(_3\)Pd\(_2\)Ge\(_6\). It is expected that the Ce ion in 4a cage with cubic symmetry \( O_h \) favors off-center positions along one of the three principle directions of [100], [110] and [111]. As one can see the cage at 4a site in Fig. 1, it is of particular interest that no atom exists along the threefold [111] directions, while the Ce atom occupies along the fourfold [100] and the Pd atom along the two-fold [110] ones. This crystallographic character may promise a flat potential along the threefold [111] directions and profound potentials along the fourfold [100] and two-fold [110] directions. Presumably the Ce ion at 4a site prefers the off-center eight positions along the [111] directions, which are defined as \( r_1 = (a, a, a) \), \( r_2 = (-a, -a, a) \), \( r_3 = (-a, -a, -a) \), \( r_4 = (a, -a, -a) \), \( r_5 = (a, a, -a) \), \( r_6 = (-a, a, -a) \), \( r_7 = (a, -a, a) \), \( r_8 = (-a, a, a) \). The atomic densities \( \rho_i = \rho_0(r_i)(i = 1 \sim 8) \) at the eight off-center positions are also defined. When 48 symmetry operators of \( O_h \) point group are acted on the atomic densities \( \rho_i \), one can derive the transfer representation matrices with \( 8 \times 8 \) elements. Consequently, one obtains the characters \( \chi_{\text{rat}}^{[11]} \) for the rattling motion by tracing the diagonal elements of the representation matrices. Using the characters \( \chi_{\text{rat}}^{[11]} \) and the character table for the irreducible representations of \( O_h \), the rattling motion over the eight off-center positions along the [111] direction is reduced to the direct sum of \( \Gamma_1(1D) \oplus \Gamma_2(1D) \oplus \Gamma_4(3D) \oplus \Gamma_5(3D) \).

Employing projection operators on appropriate atomic density \( \rho_i \), we obtain the rattling modes for the irreducible representations as listed in Table 1 together with the elastic strains \( \varepsilon_\Gamma \). One can see the presence of \( \Gamma_5 \) rattling mode \( \rho_1 = \rho_2 \) coupled to the strain \( \varepsilon_{xy} \) contrary to the absence of \( \Gamma_3 \) rattling mode coupled to the strain \( \varepsilon_u, \varepsilon_v \). This is consistent with the fact that the ultrasonic dispersion reveals in \( C_{44} \) and is absent in \( (C_{11} - C_{12})/2 \). The Ce atom in the cage of Ce\(_3\)Pd\(_2\)Ge\(_6\) obeys a harmonic oscillation of \( \zeta(z) = (1/\pi\alpha_0)1/2\exp(-z^2/2\alpha_0^2) \) with a mean square displacement \( \alpha_0 = (1/2\pi)(\hbar\gamma_0/M)^{1/2} \). The attempt time \( \tau_0 = 3.1 \times 10^{-11} \) sec and the mass \( M = 140m_p \) where \( m_p \) is a proton mass, leads to the mean square displacement \( \alpha_0 \) being approximately twice of off-center distances \( a \) as \( \alpha_0 = 2a = 0.48 \) \( \text{ Å} \).

The full symmetry \( \Gamma_1 \) rattling motion \( \rho_1 = \rho_2 \) means the uniform atomic distribution with fraction 1/8 at each eight off-center positions. While the \( \Gamma_5 \) rattling mode, for instance \( \rho_5, \rho_5, \rho_5, \rho_5 \) of Ce\(_3\)Pd\(_2\)Ge\(_6\) represents anisotropic atomic distribution being quadrupole \( \Delta \) at the lowest order such as fraction 1/4 at \( r_1, r_2, r_5, r_6 \) and zero at \( r_3, r_4, r_7, r_8 \) as shown in Fig. 15. The present group theoretical analysis for the rattling mode is essentially the same treatment previously argued for the charge fluctuation mode.\(^{24,26,32}\) In the present system Ce\(_3\)Pd\(_2\)Ge\(_6\), the thermally activated \( \Gamma_5 \) rattling mode may be a ground state and the \( \Gamma_1, \Gamma_2, \Gamma_4 \) be excited states.

Our group has recently found similar ultrasonic dispersion around 30 K in a heavy fermion superconductor PrOs\(_4\)Sb\(_{12}\) with a filled skutterudite structure. It should be noted that ultrasonic dispersion in the \( (C_{11} - C_{12})/2 \) mode of PrOs\(_4\)Sb\(_{12}\) indicates the \( \Gamma_3 \) rattling motion of Pr atom over six fractionally occupied positions along [100]. The dispersion of \( (C_{11} - C_{12})/2 \) in PrOs\(_4\)Sb\(_{12}\) is contrary to the one of \( C_{44} \) in the present compound of Ce\(_3\)Pd\(_2\)Ge\(_6\).\(^{14}\) The attempt time \( \tau_0 = 8.8 \times 10^{-11} \) sec, activation energy \( E = 168 \) K and mean square displacement \( z_0 = 0.80 \) \( \text{ Å} \) in PrOs\(_4\)Sb\(_{12}\) are comparable to the present results of Ce\(_3\)Pd\(_2\)Ge\(_6\).

The thermally activated \( \Gamma_5 \) rattling motion with fractional atomic state in Ce\(_3\)Pd\(_2\)Ge\(_6\) dies out with decreases.

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**TABLE I: Rattling modes with eight off-center positions along the three-fold [111] direction in the 4a-site cage with \( O_h \) point group symmetry. Corresponding elastic strains are also listed. There is a \( \Gamma_5 \) rattling mode coupled to the \( \varepsilon_{xy} \)-type strain of the \( C_{44} \) mode. This is contrary to the absence of the \( \Gamma_3 \) rattling mode to the \( \varepsilon_u, \varepsilon_v \) of the \( (C_{11} - C_{12})/2 \) mode. The present ultrasonic dispersion in \( C_{44} \) of Ce\(_3\)Pd\(_2\)Ge\(_6\) originates from the \( \Gamma_5 \)-type rattling at 4a site.**

| Symmetry | Rattling mode | Strain |
|----------|---------------|--------|
| \( \Gamma_1 \) | \( \rho_{1} = \rho_2 + \rho_3 + \rho_4 + \rho_5 + \rho_6 + \rho_7 + \rho_8 \) | \( \varepsilon_{u} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \) |
| \( \Gamma_2 \) | \( \rho_{2} = \rho_1 + \rho_2 + \rho_3 + \rho_4 - \rho_5 - \rho_6 - \rho_7 - \rho_8 \) | \( \varepsilon_{u} = (2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})/\sqrt{3} \) |
| \( \Gamma_3 \) | \( \rho_{3} = \rho_1 + \rho_2 - \rho_3 + \rho_4 + \rho_5 - \rho_6 + \rho_7 + \rho_8 \) | \( \varepsilon_{u} = \varepsilon_{zz} - \varepsilon_{yy} \) |
| \( \Gamma_4 \) | \( \rho_{4} = \rho_1 - \rho_2 - \rho_3 + \rho_4 + \rho_5 - \rho_6 - \rho_7 - \rho_8 \) | \( \varepsilon_{yy} \) |
| \( \Gamma_5 \) | \( \rho_{5} = \rho_1 + \rho_2 - \rho_3 - \rho_4 + \rho_5 + \rho_6 + \rho_7 + \rho_8 \) | \( \varepsilon_{xx} \) |
| \( \rho_{6} = \rho_1 + \rho_2 - \rho_3 + \rho_4 + \rho_5 + \rho_6 - \rho_7 - \rho_8 \) | \( \varepsilon_{xy} \) |
At further low temperatures, the off-center tunneling state of Ce ions in the 4a-site cages will appear, which means a quantum state being occupied four positions, for instance at $r_1$, $r_2$, $r_5$, and null at $r_3$, $r_4$, $r_7$, $r_8$. The freezing of the thermally activated motion of the $\Gamma_3$ rattling mode brings about the atomic tunneling state at low temperatures.

![Schematic view for the $\Gamma_3$ rattling mode $\rho_{\Gamma_3,xy}$ due to the off-center Ce-ion along the three-fold [111] direction in the 4a-site cage.](image)

**FIG. 15:** Schematic view for the $\Gamma_3$ rattling mode $\rho_{\Gamma_3,xy}$ due to the off-center Ce-ion along the three-fold [111] direction in the 4a-site cage. The $\rho_{\Gamma_3,xy}$ represents that fractional atomic density $1/4$ is located at $r_1$, $r_2$, $r_5$, and null at $r_3$, $r_4$, $r_7$, $r_8$. The freezing of the thermally activated motion of the $\Gamma_3$ rattling mode brings about the atomic tunneling state at low temperatures.

**IV. CONCLUDING REMARKS**

In the present paper we have measured the elastic constants and thermal expansion of Ce$_3$Pd$_{20}$Ge$_6$. The characteristic elastic softening in $(C_{11} - C_{12})/2$ and $C_{44}$ is well described in terms of the quadrupole susceptibility for the $\Gamma_8$ ground state. The important finding is that the $(C_{11} - C_{12})/2$ shows the huge softening of 50% towards $T_{Q1} = 1.25$ K and the $C_{44}$ exhibits the softening of 2.5% only. This result strongly indicates the FQ ordering with the order parameter of the $\Gamma_3$ symmetry in phase II below $T_{Q1}$. Actually we have successfully observed the sharp increase of $\Delta L/L = 1.9 \times 10^{-4}$ in length along the [001] direction below $T_{Q1}$. This is the evidence for the $O^2_3$-type FQ ordering accompanied by the structural change from cubic lattice to tetragonal one at $T_{Q1}$ in Ce$_3$Pd$_{20}$Ge$_6$.

For the investigation of the magnetic phase diagram concerning the FQ phase II and AFM phase III in Ce$_3$Pd$_{20}$Ge$_6$, the elastic constants and thermal expansion in fields have been measured. We have found that the boundary from the paramagnetic phase I to the FQ phase II of $O^2_3$ shifts to higher temperatures with increasing magnetic fields. The result that the I-II phase transition becomes obscure in fields is similar to the liquid-gas transition approaching to the critical end point under pressure. This result consistent with the fact that the FQ order parameter $O^2_3$ in Ce$_3$Pd$_{20}$Ge$_6$ has the total symmetry under fields along the [001] direction. The boundary from the phase II to the AFM ordering shifts to lower temperatures as similar as the conventional AFM ordering.

We have found the ultrasonic dispersion in the $C_{44}$ mode indicating the rattling motion with $\Gamma_3$ symmetry. Taking into account the absence of the atom along the [111] direction in 4a-site cage, we have successfully picked up the specific $\Gamma_3$ rattling mode $\rho_{\Gamma_3,yz}$, $\rho_{\Gamma_3,xx}$, $\rho_{\Gamma_3,xy}$ with the fractional atomic density over the eight minimum positions of potential along the four-fold [111], [111], [111] and [111] directions. The dispersion of the $C_{44}$ mode obeying the Debye-formula revealed the thermally activated-type relaxation time $\tau = \tau_0 \exp(E/k_B T)$ for the $\Gamma_3$ rattling mode with an attempt time $\tau_0 = 3.1 \times 10^{-11}$ sec and an activation energy $E = 70$ K. The estimated mean square displacement $\zeta_0 = 0.48$ Å for the harmonic oscillation of Ce atom leads to the distance of the potential minima along the [111] direction as $a = \zeta_0/2 = 0.24$ Å. In order to confirm the anisotropic atomic distribution in the 4a-site cage, the neutron or x-ray scattering is required. The freezing of the thermally activated motion due to the $\Gamma_3$ rattling mode with lowering temperature brings about the atomic tunneling state. By analogy of the charge glass compound Sm$_3$Te$_4$, the Ce-ion tunneling is expected at low temperatures. The ultrasonic investigation on La$_3$Pd$_{20}$Ge$_6$ free from the long-range ordering due to 4f-electrons is now in progress to shed light on the tunneling and rattling in cages.

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