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# Non-Kramers doublet ground state in a quaternary cubic compound $PrRu_2In_2Zn_{18}$ investigated by ultrasonic measurements

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We performed ultrasonic measurements on a quaternary cubic compound $PrRu_2In_2Zn_{18}$ to explore the ground state properties derived from non-Kramers $\Gamma_3$ doublet of $Pr^{3+}$. $PrRu_2In_2Zn_{18}$ is a quaternary derivative of the ternary compound $PrRu_2Zn_{20}$ that exhibits a structural phase transition at $T_S = 138$ K. In $PrRu_2In_2Zn_{18}$, the Zn atoms at the 16*c* site in $PrRu_2Zn_{20}$ are selectively replaced by In atoms. A monotonic increase was observed in the temperature dependence of elastic constants $C_L = (C_{11} + 2C_{12} + 4C_{44})/3$ and $C_T = (C_{11} - C_{12} + C_{44})/3$ in the temperature range around $T_S$ to which an elastic softening was observed in $(C_{11} - C_{12})/2$ for $PrRu_2Zn_{20}$. The disappearance of the softening indicates that the structural transition in $PrRu_2Zn_{20}$ is suppressed by the substitution of Zn ions by In ones with a larger ionic radius. Alternatively, the $C_T$ of $PrRu_2In_2Zn_{18}$ exhibits a precursor Curie-type elastic softening toward low temperatures being responsible for the non-Kramers $\Gamma_3$ ground state. We discuss the ground state and the evolution of the elastic properties of the different single-crystal samples of $PrRu_2In_2Zn_{18}$ grown under different conditions.

**Keywords:** ultrasonic measurements, non-Kramers doublet, structural phase transition, crystalline electric field effect

**PACS:** 43.35.Cg, 76.60.Gv, 82.35.Jk, 75.10.Dg **DOI:** 10.1088/1674-1056/ad35af

## 1. Introduction

Praseodymium-based cubic compounds $PrT_2X_{20}$ ($T$: transition metal, $X$ = Al and Zn) have attracted considerable attention because they exhibit various interesting phenomena arising from multipole degrees of freedom.[1–9] For example, $PrIr_2Zn_{20}$ is the first substance that shows a superconducting transition in the presence of a quadrupolar ordering.[1] In addition, a possible occurrence of quadrupole driven non-Fermi liquid state is suggested by recent experimental and theoretical studies.[2–4] $PrT_2Al_{20}$ ($T$ = Ti and V) also shows a coexistence of superconductivity and quadrupolar ordering.[5,6] For $PrTi_2Al_{20}$, a ferro-quadrupolar ordering at 2 K and a pressure induced heavy-fermion superconductivity were reported.[5,7,8] Interestingly, the superconducting transition temperature and effective electron mass are enhanced with the decrease of the quadrupolar ordering temperature by applying pressure.[8]

$PrT_2X_{20}$ crystalizes with the cubic $CeCr_2Al_{20}$-type (space group $Fd\bar{3}m$),[10] and the point group of the Pr site is cubic $T_d$. In general, the Hund's rule ground state $J = 4$ of $Pr^{3+}$ ion with $4f^2$ electrons is split into four multiplets by cubic crystalline electric field (CEF): $\Gamma_1$ singlet, non-Kramers $\Gamma_3$ doublet, and magnetic $\Gamma_4$, $\Gamma_5$ triplets. In the case of $PrT_2X_{20}$, the CEF ground state of $Pr^{3+}$ ion is a non-Kramers $\Gamma_3$ doublet which has only two kinds of multipoles, that is, quadrupole and octupole degrees of freedom.[7,11,12] Therefore, only these multipole degrees of freedom are active at temperature well below the CEF splitting energy, which could lead to fascinating multipole related phenomena such as multipole ordering, non-Fermi liquid state, and unconventional superconductivity. Among $PrT_2X_{20}$, $PrRu_2Zn_{20}$ shows a structural phase transition at $T_S = 138$ K. The multiple degrees of freedom in $PrRu_2Zn_{20}$ are lifted at $T_S$ because the $\Gamma_3$ doublet ground state is split into two singlets owing to the symmetry lowering by the structural phase transition.[15–17] In ultrasonic measurement, softening and temperature hysteresis of the elastic constant $C_E = (C_{11} - C_{12})/2$ were observed at around $T_S$.[15] In addition, the electrical resistivity shows a hysteresis behavior in the same temperature range.[16] Similar structural transitions have been observed in the nonmagnetic analog $LaT_2Zn_{20}$ ($T$ = Ru, Ir and Os),[16,18,19] which indicates that the 4f electrons are not attributed to the structural transition.

In $RT_2Zn_{20}$, there are five crystallographic site; 8*a* for *R*, 16*d* for *T*, 16*c*, 48*f*, and 96*g* for Zn. The first principles and inelastic x-ray scattering studies suggest that the structural phase transition in $RRu_2Zn_{20}$ is caused by the low-energy vibration of Zn atoms at the 16*c* site [Zn(16*c*)], which is surrounded by an atomic cage consisting of 2*R* and 12Zn atoms at the 96*g* site [Zn(96*g*)].[20–22] In fact, the cubic phase is stabilized when the displacement parameter of Zn(16*c*) is reduced by the replacement of *R* atoms.

Recently, a new ordered variant of the $CeCr_2Al_{20}$-type with the chemical formula $RT_2A_2Zn_{18}$ ($R$ = rare-earth; $T$ = Co, Fe, and Ru, $A$ = Sn and In) was reported by Ishikawa *et al.* and our group.[23–26] In these compounds, Zn(16*c*) in $RT_2Zn_{20}$ is selectively replaced by Sn or In atoms.[25] Interestingly, for $RRu_2Sn_2Zn_{18}$, the structural transition in $RRu_2Zn_{20}$ is suppressed by replacement of Zn(16*c*) by Sn.[24,25] Since

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the structural phase transition is suppressed, the non-Kramers doublet ground state is maintained, and thus the multipole degrees of freedom are still active even at low temperatures.[24] On the other hand, the CEF ground state of isostructural $PrRu_2In_2Zn_{18}$ has not been examined so far. A van-Vleck paramagnetic behavior is observed by magnetic susceptibility measurement, which indicates that the CEF ground state is non-magnetic, namely $\Gamma_1$ singlet or $\Gamma_3$ doublet if the structural phase transition is suppressed by the In substitution as found in $PrRu_2Sn_2Zn_{18}$.[26]

Ultrasonic measurement is a powerful technique to determine the CEF ground state because a precursor Curie-type elastic softening is highly expected if a CEF ground state possesses quadrupole degrees of freedom.[12–14] In addition, in the previous study for Sn-substituted $PrRu_2Zn_{20}$, it was reported that the molar ratio Sn/Zn on synthesis is important for selective replacement of Zn(16*c*) by Sn, and atomic disorder arising from the incomplete replacement affects strongly the 4f electronic state.[24] Therefore, we concern the prime issue of whether the 4f electronic state is affected by the molar ratio In/Zn on synthesis. We measure the longitudinal elastic constant $C_L = (C_{11} + 2C_{12} + 4C_{44})/3$ and transverse elastic constant $C_T = (C_{11} - C_{12} + C_{44})/3$ by applying the ultrasonic wave propagating along $\langle 111 \rangle$ direction. Considering the symmetry of the elastic moduli and quadrupole moments, it can be highly expected that $C_T$ shows a softening, whereas $C_L$ does not if $\Gamma_3$ doublet is the ground state. This distinctness helps us to determine the 4f ground state of $Pr^{3+}$ ions in this system. As mentioned below, we observe a precursor Curie-type elastic softening of $C_T$ of $PrRu_2In_2Zn_{18}$ below 10 K, indicating that the CEF ground state is a non-Kramers $\Gamma_3$ doublet. In this paper, the ground state and the evolution of their elastic properties of the different single-crystal samples grown under different conditions: $PrRu_2In_2Zn_{18}$ (#1 and #2) are reported, and the substitution effect on elastic and ground state properties is discussed.

## 2. Experimental details

Single crystalline samples of $PrRu_2In_2Zn_{18}$ were prepared by the self-flux method. The pure elements of Pr(99.9%), Ru(99.9%), In(99.99%), and Zn(99.9999%) were used as raw materials. In the previous study concerning Sn-substituted $PrRu_2Zn_{20}$, it was found that the starting ratio Sn/Zn on synthesis is important for selective replacement of Zn(16*c*) by Sn. Thereby, in this study, we employed two different starting ratios of Zn and In: #1 (Pr:Ru:In:Zn = 1:2:10:30) and #2 (Pr:Ru:In:Zn = 1:2:5:35) to reveal whether the initial ratio on synthesis affects the selective substitution of In to the 16*c* site. X-ray diffraction on single crystals was conducted to confirm the crystallographic structure and quality of the samples. Atomic compositions were determined by x-ray fluorescence analysis. The results confirmed that In atoms are substituted into the samples used for the measurement of physical properties.

The elastic constants were measured by the phase-comparison type pulse-echo method from 100 K to 150 K using $N_2$ dewar, and from 2 K to 10 K using quantum design PPMS. Plates of $LiNbO_3$ were used as a piezoelectric transducer, and they were glued on the parallel planes of the sample by an elastic polymer Thiokol. The surface of sample was polished by polishing papers to improve the propagation efficiency of ultrasonic waves. The size of the sample used in this study is not enough large and only the crystallographic parallel planes (111) are available. In consequence, we could measure and show only elastic constants, $C_L = (C_{11} + 2C_{12} + 4C_{44})/3$ and $C_T = (C_{11} - C_{12} + C_{44})/3$ by applying longitudinal and transverse ultrasonic waves propagating along the $\langle 111 \rangle$ direction.

## 3. Experimental result and discussions

Figure 1(a) shows the temperature dependence of the longitudinal elastic constant $C_L$ of #1 and #2 in the temperature range between 100 K and 150 K, giving particular attention to the interval temperatures containing a possible structural phase transition. For clarity, each curve is shifted by an arbitrary offset on the vertical scale. $C_L$ increases with decreasing temperature down to 100 K. However, #1 shows a temperature hysteresis between 100 K and 130 K. Similar results are obtained by measurements of the transverse elastic constant $C_T$ as shown in Fig. 1(b). This hysteresis behavior indicates that the structural phase transition is partially not suppressed in #1. The incomplete suppression of the structural phase transition may result from the inhomogeneity of In substitution. For example, it is possible that some of Zn(16*c*) is not replaced by In atom, and/or In atoms are substituted not only to the 16*c* site but also to the other Zn sites. In fact, we reported previously that in $PrRu_2Sn_2Zn_{18}$, the Sn atoms are substituted to not only the 16*c* site but also other Zn sites depending on the sample synthesis condition. Since the hysteresis behavior is not observed in #2, it is expected that the Zn(16*c*) is more selectively replaced by In in #2 than in #1. It should be noted here that the hysteresis loop appeared around $T_s$ shows opposite behavior regarding a temperature sweep comparing $PrRu_2In_2Zn_{18}$ to $PrRu_2Sn_2Zn_{18}$. We confirm the repeatability and reproducibility of the results. A metastable state of a first-order phase transition would be realized around $T_s$ for both systems. This is an unsettled issue.

Let us next move on low-temperature behavior of $C_L$ and $C_T$ for both #1 and #2 below 20 K to examine the CEF ground state property. All the elastic constants increase monotonically with decreasing the temperature below around 150 K to 20 K. Figures 2(a) and 2(b) show the temperature dependence of the

elastic constants $C_L$ and $C_T$ for the samples #1 and #2 below 20 K. For clarity, each curve is shifted by an arbitrary offset on the vertical scale. $C_L$ increases monotonically with decreasing temperature down to around 2 K. On the other hand, $C_T$ shows an elastic softening below 8 K, being proportional to reciprocal temperature at low temperatures, as discussed below in detail.

It is well-known that the elastic softening proportional to the reciprocal temperature is observed when the symmetry of the strain induced by the ultrasonic wave corresponds to the symmetry of the relevant quadrupole moment. In general, $C_L$ can be described as a linear combination of the bulk modulus $C_B = (C_{11} + 2C_B)/3$ with $\Gamma_1$ symmetry and the $C_{44}$ mode with $\Gamma_5$ symmetry. On the other hand, the composite elastic constant $C_T$ can be expressed as a linear combination of the $(C_{11} - C_{12})/2$ mode with $\Gamma_3$ symmetry and the $C_{44}$ mode with $\Gamma_5$ symmetry. As mentioned above, the Hund's rule ground state $J = 4$ of $Pr^{3+}$ ion is generally split into four multiplets under the cubic crystalline electric field (CEF): $\Gamma_1$ singlet, non-Kramers $\Gamma_3$ doublet, and magnetic $\Gamma_4$, $\Gamma_5$ triplets. Among these multiplets, both of $\Gamma_1$ singlet and non-Kramers $\Gamma_3$ doublet have no magnetic dipole moments, whereas $\Gamma_3$ doublet has the $\Gamma_3$ type quadrupole moments: $O_2^0$ and $O_2^2$. On the other hand, magnetic $\Gamma_4$ and $\Gamma_5$ triplets have magnetic moments and $\Gamma_5$ type quadrupole moments: $O_{xy}$, $O_{yz}$, and $O_{zx}$ in addition to the $\Gamma_3$ type quadrupole moments. Therefore, when the CEF ground state is $\Gamma_3$ doublet, a Curie-type elastic softening of $C_T$ is expected, whereas the softening does not appear in $C_L$. For the reasons mentioned above, it is reasonable to suppose that the $\Gamma_3$ non-Kramers CEF doublet ground state is realized in $Pr^{3+}$ ions in $PrRu_2In_2Zn_{18}$.

As mentioned in the Introduction, non-In substituted compound $PrRu_2Zn_{20}$ shows a softening and temperature hysteresis of elastic constant $C_E = (C_{11} - C_{12})/2$ at around $T_S$ = 138 K due to the structural transition. The disappearance of the softening indicates that the structural phase transition in $PrRu_2Zn_{20}$ is suppressed by In substitution. What needs to be emphasized here is that no precursor elastic softening toward $T_s$ is observed in the temperature dependence of the principal elastic constants in the isomorphous referenced system $LaRu_2Zn_{20}$.[18] However, an ultrasonic study reported by Ishii *et al*. demonstrates that the elastic constant $(C_{11} - C_{12})/2$ shows a pronounced softening below $\sim$ 250 K down to $T_s$ for $PrRu_2Zn_{20}$. From this experimental fact, they claim that the softening below 250 K is caused by the strain-quadrupole and quadrupole–quadrupole interactions. The role of 4f electronic state in the driving mechanism at the structural phase transition is still an unsettled issue. Nevertheless, it is quite likely that the anharmonic dynamics of Zn ions at the 16*c* site would contribute to the structural transition for $PrRu_2Zn_{20}$.

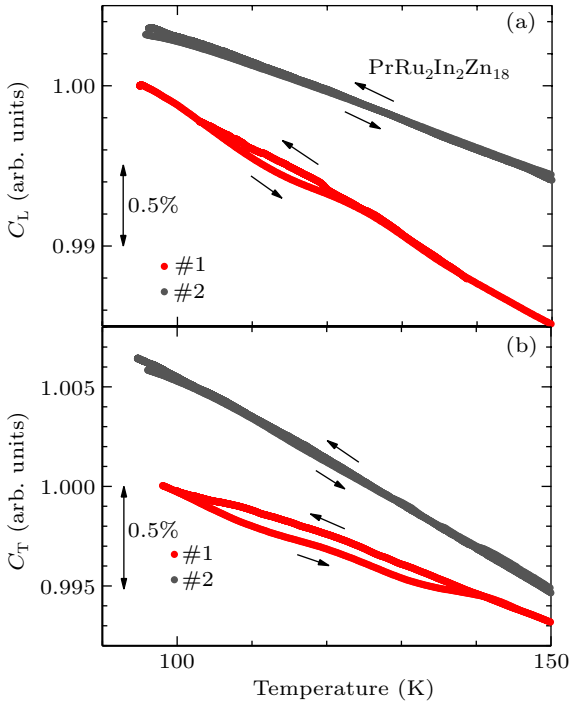



**Fig. 1.** Temperature dependence of the relative variation of (a) the longitudinal elastic modulus $C_L = (C_{11} + 2C_{12} + 4C_{44})/3$ and (b) the transverse elastic constants $C_T = (C_{11} - C_{12} + C_{44})/3$ of the both samples #1 and #2. $PrRu_2In_2Zn_{18}$ in the temperature region from 100 K to 150 K in which the structural phase transition takes place in the mother material, $PrRu_2Zn_{20}$. For clarity each curve is shifted by an arbitrary offset on the vertical scale.

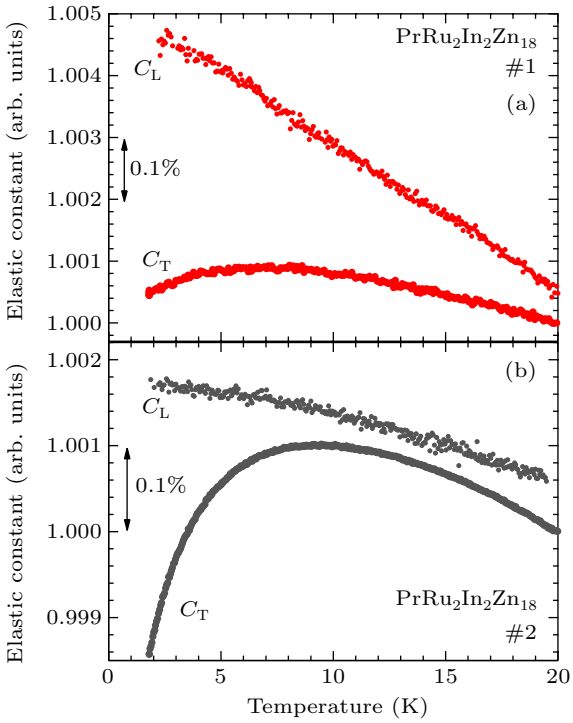



**Fig. 2.** Temperature dependence of the relative variation of the elastic constants $C_L = (C_{11} + 2C_{12} + 4C_{44})/3$ and $C_T = (C_{11} - C_{12} + C_{44})/3$ of (a) #1, and (b) #2 below 20 K. For clarity each curve is shifted by an arbitrary offset on the vertical scale.

In addition, the present results also agree with those of the previous magnetic susceptibility measurement. In the measurement, a van-Vleck paramagnetic behavior is observed,

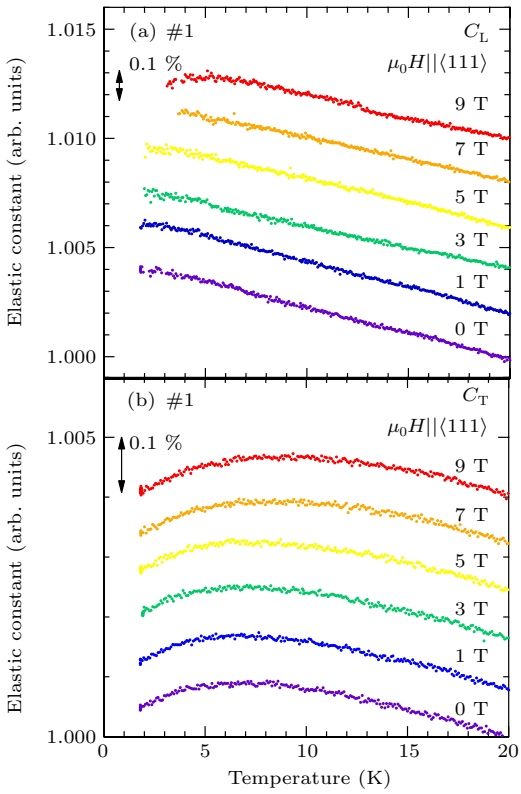



**Fig. 3.** Temperature dependence of the relative variation of (a) the longitudinal $C_L$ and (b) transverse $C_T$ elastic constants of the #1 sample below 20 K under several magnetic fields applied along the $\langle 111\rangle$ axis, parallel to the propagation direction of the sound waves. Offset for clearly in ascending order from bottom to top.

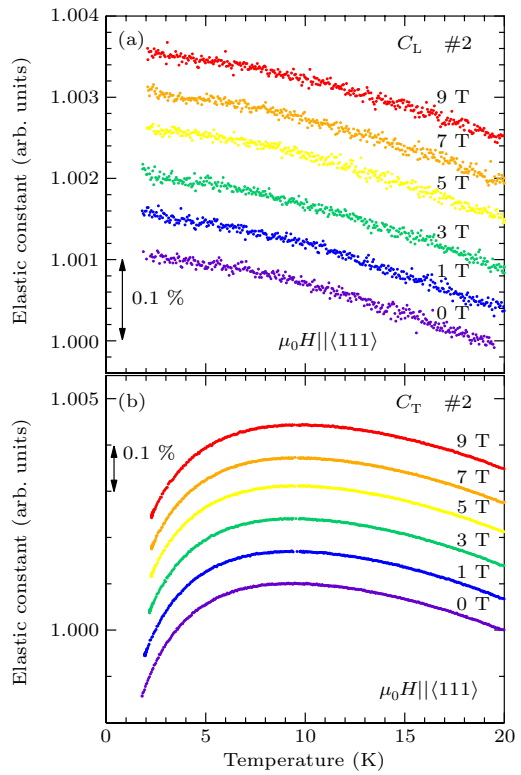



**Fig. 4.** Temperature dependence of the relative variation of (a) the longitudinal $C_L$ and (b) transverse $C_T$ elastic constants of the #2 sample below 20 K under several magnetic fields applied along the $\langle 111\rangle$ axis, parallel to the propagation direction of the sound waves, offset for clearly in ascending order from bottom to top.

which indicates that the CEF ground state is non-magnetic, namely non-magnetic $\Gamma_1$ singlet or non-Krmaers $\Gamma_3$ doublet. Since the $\Gamma_1$ singlet possesses no quadrupole moments, it is expected that both of $C_L$ and $C_T$ do not show any elastic softening if $\Gamma_1$ singlet is the ground state. Therefore, the softening of $C_T$ in $PrRu_2In_2Zn_{18}$ indicates that CEF ground state would be $\Gamma_3$ doublet (not $\Gamma_1$ singlet). Figures 3 and 4 show the temperature dependence of $C_L$ and $C_T$ of #1 and #2, respectively under several magnetic fields applied along the $\langle 111\rangle$ direction up to $\mu_0H = 9$ T, offset for clearly in ascending order from bottom to top. Both of the $C_L$ and $C_T$ do not show distinct magnetic field dependence. The small magnetic field effect agrees with the non-magnetic CEF ground state, and may indicate that the Zeeman splitting of the $\Gamma_3$ doublet is small when $\mu_0H\|\langle 111\rangle$. In general, the degree of Zeeman splitting is closely related to the CEF parameters; therefore the small magnetic field dependence for $\mu_0H\|\langle 111\rangle$ may help us to determine the CEF parameters of $PrRu_2In_2Zn_{18}$ by other measurements, such as neutron scattering, and NMR measurements.

Let us here discuss the ground state and elastic properties of the mother compound $PrRu_2Zn_{20}$. Figure 5(a) exhibits the calculated results of the temperature dependence of $(C_{11}-C_{12})/2$ and $C_{44}$ based on the following single-ion quadrupolar strain susceptibility formula $\chi^s_{\Gamma_i}(T)$:

$$\chi^s_{\Gamma_i}(T) = \sum_{i,k} \frac{\exp(\frac{-E^{(0)}_{ik}}{k_BT})}{Z} \times \left( \frac{1}{k_BT} |\langle ik| O_{\Gamma_i} |ik\rangle|^2 - 2\sum_{j,l} \frac{|\langle ik| O_{\Gamma_i} |jl\rangle|^2}{E_i - E_j} \right),$$

where, $\chi^s_{\Gamma_i}$ represents $\chi^s_{\Gamma_3}$ and $\chi^s_{\Gamma_5}$, which are proportional to $C_E = (C_{11}-C_{12})/2$ and $C_{44}$ as $C_E \propto -\chi^s_{\Gamma_3}, C_{44} \propto -\chi^s_{\Gamma_5}$, respectively. $O_{\Gamma_i}$, $Z$, $\langle ik|$ and $E^{(0)}_{ik}$ represent a quadrupolar operator, the partition function, the $k$-th eigenfunction and eigenvalue (eigenenergy) of the $i$-th CEF level, respectively. The Hamiltonian used to describe the single-ion quadrupolar strain susceptibility $\chi^s_{\Gamma_i}(T)$ is expressed as

$$\mathcal{H} = \mathcal{H}_{CEF} + \mathcal{H}_{Zeeman}.$$

As mentioned already, $PrRu_2Zn_{20}$ crystallizes in a cubic structure represented by the space group $Fd\bar{3}m$, in which the local symmetry at the Pr ion site is $T_d(\bar{4}3m)$. The Hamiltonian for the CEF potential at the Pr site is described as follows:

$$\mathcal{H}_{CEF} = W\left[\frac{x}{60}(O^0_4 + 5O^4_4) + \frac{1-|x|}{1260}(O^0_6 - 21O^4_6)\right],$$

where $O^n_m$ are Stevens operators. Here we use the proposed CEF parameters $W = -0.054$ meV and $x = 0.02$ determined by the inelastic neutron scattering measurement mentioned below in detail.[11] Furthermore, the Hamiltonian for the Zeeman

coupling with the applied magnetic field $\boldsymbol{H}$ and the total angular momentum $\boldsymbol{J}$ is described as follows:

$$\mathcal{H}_{\text{Zeeman}} = -g_J \mu_B \boldsymbol{J} \cdot \boldsymbol{H},$$

where $g_J$ and $\mu_B$ are the Landé $g$ factor and Bohr magneton, respectively. Using a set of basis wave functions for the total angular momentum $J = 4$ for the $4f^2$ configuration, we diagonalize the Hamiltonian $\mathcal{H}$ to obtain eigenstate wave functions $|ik\rangle$.

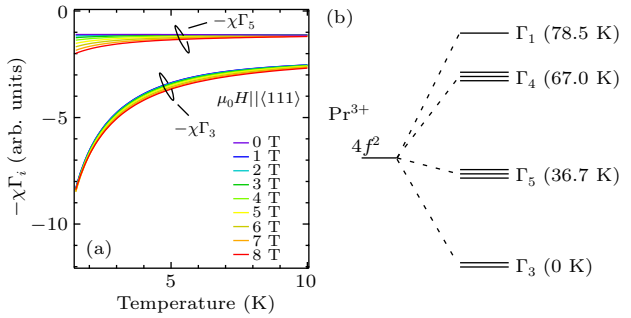



**Fig. 5.** (a) Theoretical results of the temperature dependence of the single-ion quadrupolar strain susceptibility $\chi^s_{\Gamma_i}(T)$ ($\Gamma_i$ : $\Gamma_3$ and $\Gamma_5$) in selected magnetic fields along the $\langle 111 \rangle$ axis. Their offsets are shifted arbitrarily for clarity. (b) The proposed model of the CEF level scheme of the 4f electronic state of $PrRu_2Zn_{20}$.

In the present case of $PrRu_2Zn_{20}$, the first term, i.e., Curie term in the single-ion quadrupolar strain susceptibility $\chi^s_{\Gamma_i}(T)$ due to the $\Gamma_3$ non-Kramers doublet ground state, gives rise to the elastic softening proportional to reciprocal temperature at low temperatures. The solid curves in Fig. 5(a) are calculated results based on the level scheme proposed by the inelastic neutron scattering studies as follows: $\Gamma_3\,(0\,\text{meV}) - \Gamma_5\,(3.16\,\text{meV}) - \Gamma_4\,(4.480\,\text{meV}) - \Gamma_1\,(7.59\,\text{meV})$, as shown in Fig. 5(b). The obtained elastic constants as shown in Figs. 3 and 4 are well reproduced by this proposed CEF level scheme, again suggesting that the magnetic-field insensitive elastic softening would be due to the small Zeeman splitting of the $\Gamma_3$ non-Kramers doublet ground state.

Next, we discuss the sample dependence of the elastic softening observed in $C_T$. Figure 6 shows a comparison of the temperature dependence of elastic modulus $C_T$ of #1 and #2. The solid lines denote the calculation results based on the formula described in detail below. If the elastic softening really comes from the non-Kramaers $\Gamma_3$ doublet, the result can be understood with the following formula:[27–29]

$$C_\Gamma = C^0_\Gamma(T) - \frac{N g^2_\Gamma \chi^s_\Gamma}{1 - g'_\Gamma \chi^s_\Gamma}. \tag{1}$$

Here, $N$ is the number of Pr ions in unit volume and $C^0_\Gamma(T)$ and $\chi^s_\Gamma$ denote the background without quadrupolar-strain interaction and the quadrupolar susceptibility for the 4f electronic state in the CEF potential, respectively. The $g_\Gamma$ denotes the coupling constant between elastic strain and quadrupolar moment with $\Gamma$ symmetry in which $\Gamma$ represents the irreducible representation of the point group, i.e., $\Gamma_3$ here. On the other hand, the $g'_\Gamma$ denotes the coupling constant between quadrupolar moments with $\Gamma$ symmetry, which is proportional to the quadrupolar interaction between $Pr^{3+}$ ions. For the both mother and present systems, $PrRu_2Zn_{20}$ and $PrRu_2In_2Zn_{18}$, the non-Kramaers $\Gamma_3$ doublet would be realized and dominant in the quadrupolar susceptibility at low temperatures. In this case, the above formula can be rewritten as follows by using $\chi^s_\Gamma = A_\Gamma/T$ in which $A_\Gamma$ is the Curie constant of the quadrupolar susceptibility $\chi^s_\Gamma$:[30,31]

$$C_\Gamma = C^0_\Gamma(T) - \frac{N g^2_\Gamma A_\Gamma}{T - g'_\Gamma A_\Gamma} = C^0_\Gamma(T) - \frac{N g^2_\Gamma A_\Gamma}{T - T^*}. \tag{2}$$

For simplicity, we consider here only the Curie term in the formula, where $A_{\Gamma_3}$ and $g_{\Gamma_3}$ are fitting parameters. $A_{\Gamma_3}$ is proportional to the matrix element $|\langle ik|O_{\Gamma_3}|ik\rangle|$. It is noted that if the degeneracy of the non-Kramers doublet is lifted, $A_{\Gamma_3}$ becomes smaller depending on the value of the energy-level splitting $\Delta$ between the two singlets of $\Gamma_3$ doublet. As shown in Fig. 6, the fitting curve gives us the parameters of $T^* = g'_\Gamma A_\Gamma = -3.5$ K and $-0.7$ K for #1 and #2, respectively. This result implies that the antiferro quadrupolar interaction among quadrupolar moments with $\Gamma_3$ symmetry develops at low temperatures. Again, the reasonable fitting would suggest the 4f ground state of $Pr^{3+}$ ions in $PrRu_2In_2Zn_{18}$ to be a non-Kramers $\Gamma_3$ doublet. At present we do not have a clear reason why the absolute value of $T^*$ for #1 is larger than that for #2. Since a structural phase transition would occur in the system #1 it retains cubic symmetry less compared with that in the system #2. This situation would lead us to the opposite result, i.e., $T^*(\#2) > T^*(\#1)$ due to the lift of degenerate non-Kramers $\Gamma_3$ doublet. It remains a controversial issue.

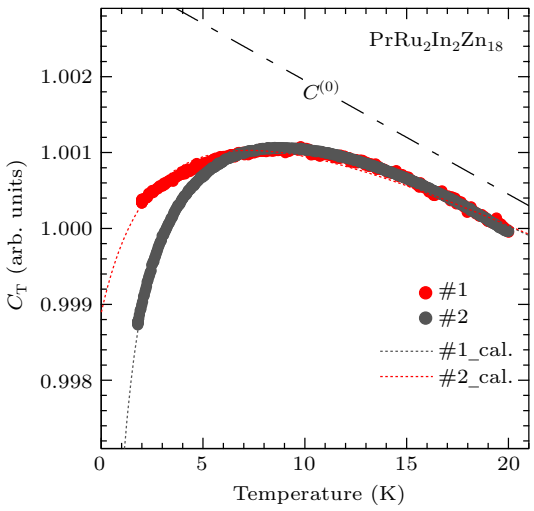



**Fig. 6.** Temperature dependence of the relative variation of the transverse elastic constant $C_T$ below 20 K for #1 (red solid circles) and #2 (black solid circles) in zero field and the calculated results for #1 (red dotted line) and #2 (black dotted line) based on the formula (2) in the text. $C^{(0)}$ denotes the background without quadrupolar-strain interaction.

Next, we would like to discuss the elastic anomaly (elastic softening) observed in the both samples #1 and #2. The magnitude of the softening in #2 is distinctly larger than that in #1. The difference of the softening ratio is probably related to the incomplete suppression of the structural transition found in #1. As discussed above, in #1, inhomogeneity of In substitution is suggested by the temperature hysteresis of $C_{\rm L}$ and $C_{\rm T}$. It is, thus expected that the lattice distortion due to both the atomic disorder and structural change affects the 4f electronic state. In fact, it has been reported that the non-Kramers doublet splits into singlet states by atomic disorder. The ground state doublet in #1 is probably partially split by the atomic disorder, leading to the suppression of the softening because the quadrupole degrees of freedom also should be partially lifted. Present results indicate that the degree of the suppression of the structural transition in $PrRu_2In_2Zn_{18}$ is strongly influenced by the sample synthesis condition as found in Sn substituted $PrRu_2Zn_{20}$, and the low-temperature properties are governed by the $\Gamma_3$ doublet ground state. On the other hand, it seems that phenomena arising from quadrupolar degrees of freedom would appear below 2 K since #2 does not show the hysteresis behavior in the temperature range between 100 K and 150 K. To confirm this scenario, the same measurements of $C_{\rm L}$ and $C_{\rm T}$ below 2 K are now on progress.

Finally, we would like to make a comment on the magnetic-field insensitive elastic softening observed in the temperature dependence of the elastic constants $C_{\rm T}$ under magnetic fields applied along the $\langle 111 \rangle$. Although the explicit 4f–CEF level scheme of Pr ions has not yet been determined, the observation of the softening suggests strongly that the ground state would be the non-Kramers doublet. We infer that the smaller In-atoms substitution replaced by the Zn atoms would retain the cubic-structure, leading to non-splitting Kramers doublet derived from 4f-electrons of Pr ions. The present results add to the experimental indications that a close relation between the structural phase transition and the elastic softening at low temperatures, in which more suppress the structural phase transition by doping In atoms, more significant the elastic softening becomes. The instability with crystal- or/and cage- structures seems to be a key mechanism for understanding the non-Kramers doublet property.

## 4. Conclusions

We present the ground state and elastic properties of the single crystalline samples $PrRu_2In_2Zn_{18}$ grown under different conditions. We measure the elastic constants $C_{\rm L} = (C_{11} + 2C_{12} + 4C_{44})/3$ and $C_{\rm T} = (C_{11} - C_{12} + C_{44})/3$ by ultrasonic measurements. The monotonic increase of the temperature dependence of $C_{\rm L}$ and $C_{\rm T}$ in the temperature range between 100 K and 150 K indicates that the structural phase transition in $PrRu_2Zn_{20}$ is suppressed by In substitution. The precursor Curie-type elastic softening towards low temperatures is observed in the temperature dependence of the $C_{\rm T}$ below around 8 K, suggesting the ground state of $Pr^{3+}$ to be the non-Kramers $\Gamma_3$ doublet. We find experimentally the close relationship of the elastic behavior between around the structural phase transition temperature and below around 8 K. Our results demonstrate experimentally the importance of the Zn (16*c*) site substitution to characterize its structural property and the associated consequences for understanding the ground state property derived from the non-Kramers double $\Gamma_3$ state of $Pr^{3+}$ ions in this family. This finding suggests that $PrRu_2In_2Zn_{18}$ is a new good playground to study the quadrupole driven phenomena found in non-Kramers doublet ground state systems.

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