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# Multipole effects of $\Gamma_3$ doublet–$\Gamma_4$ triplet states in $PrMg_3$

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Elastic properties of cubic $PrMg_3$ with a non-Kramers $\Gamma_3$ doublet ground state have been investigated with ultrasonic measurements. The temperature dependence of the elastic constant $(C_{11}-C_{12})/2$ in $PrMg_3$ exhibits a characteristic minimum around 28 K and successively shows pronounced softening below 8 K down to 20 mK. The observation is well described by multipole susceptibility considering both an electric quadrupole $O_v$ and electric hexadecapole $H_v$ with $\Gamma_{3g}$ representation for the crystal field level $\Gamma_3$ ground state and $\Gamma_4$ triplet excited state located at 54 K for $PrMg_3$. The contribution of the hexadecapole in the $\Gamma_3$-$\Gamma_4$ system to the multipole susceptibility should be emphasized to explain a common feature of the minimum typically observed in $(C_{11}-C_{12})/2$ of Pr-based compounds $PrPb_3$, $PrAg_2In$, and the present $PrMg_3$, as revealed by systematic ultrasonic measurements.

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## I. INTRODUCTION

Rare-earth compounds based on Pr ions with $4f^2$ orbits have received much attention, because exotic phenomena associated with quadrupole ordering, heavy-fermion quasiparticles, unconventional superconductivity, and rattling of guest Pr ions in a cage have been recently reported.[1–4] A cubic crystal electric field (CEF) splits the Hund's ground multiplet $^3H_4$ ($J = 4$) of $Pr^{3+}$ into a $\Gamma_1$ singlet, $\Gamma_3$ doublet, and $\Gamma_4$ and $\Gamma_5$ triplets.[5] The non-Kramers $\Gamma_3$ doublet with a special unitary group SU(2) possesses two electric quadrupoles $O_u$ and $O_v$ with $\Gamma_{3g}$ representation and a magnetic octupole $T_{xyz}$ with $\Gamma_{2u}$.[6–8] The subscript $g$ ($u$) on $\Gamma$ refers to even (odd) parity under time reversal. It should be noted that the $\Gamma_3$ doublet is free from magnetic dipoles $J_x$, $J_y$, and $J_z$ with $\Gamma_{4u}$. Therefore, the nonmagnetic $\Gamma_3$ ground state is almost independent of magnetic susceptibility at low temperatures. On the other hand, an elastic constant $(C_{11}-C_{12})/2$ in Pr-based compounds with the $\Gamma_3$ ground state is generally expected to show low-temperature softening, because the $(C_{11}-C_{12})/2$ is responsible for a quadrupole susceptibility of $O_v$ with $\Gamma_{3g}$ based on CEF levels.

The degenerate $\Gamma_3$ ground state system is expected to undergo a long-range ordered state associated with a quadrupole at low temperatures, which is clearly distinguished from the magnetic ordered state. Actually, quadrupole orderings are realized in PrPtBi and $PrPb_3$ with the site symmetry $T_d$ and $O_h$, respectively. PrPtBi shows a ferro-type quadrupole ordering at $T_Q = 1.35$ K associated with a structural phase transition to tetragonal symmetry.[9,10] $PrPb_3$ exhibits an antiferro-quadrupole ordering with sinusoidal modulation at $T_Q = 0.4$ K.[1,11–14] In these compounds, the elastic constant $(C_{11}-C_{12})/2$ commonly displays considerable softening with decreasing temperature caused by the $\Gamma_3$ ground state and turns to increase below the quadrupole transition points because of lifting the degeneracy of the $\Gamma_3$ doublet.[9,14] In addition, it was pointed out that a minimum around 7 K in $(C_{11}-C_{12})/2$ of $PrPb_3$ is attributed to an electric hexadecapole $H_v$ with $\Gamma_{3g}$ of $\Gamma_3$ doublet (0 K)–$\Gamma_4$ triplet (14.7 K)–$\Gamma_5$ triplet (28.3 K)–$\Gamma_1$ singlet (35.3 K).[14]

Among Pr-based compounds with the $\Gamma_3$ ground state, $PrAg_2In$ and $PrMg_3$ with the site symmetry $O_h$ are known to exhibit no sign of long-range ordering at low temperatures. $PrAg_2In$ shows a broad peak at 0.4 K with a huge specific heat coefficient $C/T = 6.5$ J/(mol $K^2$) without any anomaly indicating a long-range ordering down to 50 mK.[15] The elastic constant $(C_{11}-C_{12})/2$ of $PrAg_2In$ shows softening below 10 K owing to the $\Gamma_3$ ground state possessing the quadrupole $O_v$. Furthermore, the $(C_{11}-C_{12})/2$ reveals a minimum around 35 K. This minimum is not described by the quadrupole susceptibility of $O_v$ based on the CEF level scheme with $\Gamma_3$ doublet (0 K)–$\Gamma_4$ triplet (71 K)–$\Gamma_5$ triplet (96 K)–$\Gamma_1$ singlet (176 K). On further lowering the temperature, the $(C_{11}-C_{12})/2$ begins to slightly increase with a $-\log T$ dependence below 90 mK.[6]

$PrMg_3$ is also known as the $\Gamma_3$ ground state system with a level scheme $\Gamma_3$ doublet (0 K)–$\Gamma_4$ triplet (56 K)–$\Gamma_1$ singlet (135 K)–$\Gamma_5$ triplet (183 K).[16,17] $PrMg_3$ possesses a Heusler structure similar to $PrAg_2In$ where both Ag and In sites are substituted by Mg. The specific heat of $PrMg_3$ exhibits a pronounced broad peak around 0.9 K with a huge specific heat coefficient $C/T = 2.8$ J/(mol $K^2$) and indicates no sign of long-range ordering.[18] The magnetic susceptibility of $PrMg_3$

 

reveals a deviation from a van Vleck term due to off-diagonal magnetic transitions from the $\Gamma_3$ ground state to the $\Gamma_4$ excited state.[18,19] However, the characteristic feature of the elastic constant due to the $\Gamma_3$ ground state of $PrMg_3$ has not been investigated yet.

In the present paper, we report the elastic properties of $PrMg_3$ by emphasizing the characteristic behavior of $(C_{11}-C_{12})/2$. In Sec. II, sample preparation of $PrMg_3$ and ultrasonic measurements at low temperatures are described. The characteristic minimum and the low-temperature softening of $(C_{11}-C_{12})/2$ in $PrMg_3$ are presented and analyzed in terms of multipole susceptibility including electric hexadecapole as well as electric quadrupole in Sec. III. The common features of the minimum in $(C_{11}-C_{12})/2$ of $PrMg_3$, $PrPb_3$, and $PrAg_2In$ with $\Gamma_3$-$\Gamma_4$ states are discussed in Sec. III. A summary is presented in Sec. IV.

## II. EXPERIMENTS

Single crystals of $PrMg_3$ were grown using the Bridgman method with a sealed Mo crucible. An x-ray photograph using a Laue camera was used to determine the orientation of the crystal axes. We prepared two single-crystal specimens of $PrMg_3$ No. 2 and No. 3 in the present experiment. The surfaces of the samples for the ultrasonic measurements were carefully polished to be plane parallel.

The temperature dependence of ultrasonic velocity was measured by a homemade apparatus based on a phase comparator of double-balanced mixers. Ultrasonic waves were generated and detected by piezoelectric plates of $LiNbO_3$ bonded on plane-parallel surfaces of the specimen. We used 36° Y-cut plates for longitudinal ultrasonic waves and X-cut plates for transverse waves. The absolute velocity $v$ was obtained by measuring a delay time for a sequence of ultrasonic echoes with an accuracy of a few percent. Elastic constants of $C = \rho v^2$ were estimated by mass density $\rho = 3.485$ g/cm$^3$ for $PrMg_3$ with a lattice constant $a = 0.7415$ nm.

A $^3$He-$^4$He dilution refrigerator (Kelvinox, TLM) was employed for low-temperature ultrasonic measurements below 800 mK down to 20 mK, and a homemade $^3$He refrigerator was used for relatively higher temperature measurements above 450 mK. The temperature of the samples was measured by Cernox thin-film resistance cryogenic temperature sensors for the 140 K to 450 mK region and $RuO_2$ resistances for 800 mK to 20 mK.

## III. RESULTS AND DISCUSSION

### A. Elastic constants of $PrMg_3$

The temperature dependence of the elastic constants $C_{11}$, $C_B$, $C_{44}$, and $(C_{11}-C_{12})/2$ in $PrMg_3$ (No. 2) is shown in Fig. 1. The $C_{11}$ was measured by longitudinal sound waves with frequencies of 16 MHz with a propagation vector $\boldsymbol{k} \parallel [001]$ and a polarization vector $\boldsymbol{u} \parallel [001]$. The $C_{11}$ shows a softening below 70 K with decreasing temperature and reveals a broad minimum around 28 K. The softening in $C_{11}$ is again observed below 10 K down to 450 mK. The $(C_{11}-C_{12})/2$ measured by transverse sound waves with frequencies of 120 MHz with $\boldsymbol{k} \parallel [110]$ and $\boldsymbol{u} \parallel [1\bar{1}0]$ also exhibits a softening below 100 K with the characteristic minimum around 28 K similar to $C_{11}$ and again shows a softening below 8 K. The softening in $(C_{11}-C_{12})/2$ causes that of $C_{11}$.

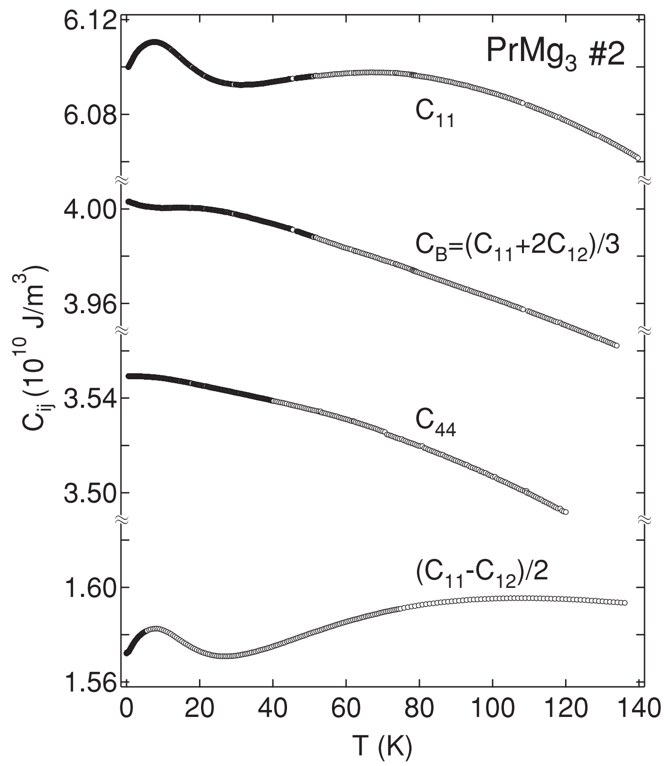


FIG. 1. Temperature dependence of the elastic constants $C_{11}$, $C_B$, $C_{44}$, and $(C_{11}-C_{12})/2$ in $PrMg_3$ (No. 2).

The transverse elastic constant $C_{44}$ obtained using transverse sound waves with frequencies of 120 MHz with $\boldsymbol{k} \parallel [001]$ and $\boldsymbol{u} \parallel [100]$ shows a monotonic increase with decreasing temperature without anomalies. This result is accounted for by the fact that the $\Gamma_3$ doublet has no diagonal elements for the $O_{xy}$-type quadrupole with $\Gamma_{5g}$ as $\langle \Gamma_3 | O_{xy} | \Gamma_3 \rangle = 0$.

The bulk modulus $C_B$ is calculated from the experimental results by using a relation $C_B = C_{11} - 2(C_{11}-C_{12})/3$. The $C_B$ reveals a monotonic increase with decreasing temperature, which indicates no anomaly in the volume change of $PrMg_3$.

In Fig. 2, we present the temperature dependence of $(C_{11}-C_{12})/2$ in $PrMg_3$ (No. 3), which is consistent with the result in $PrMg_3$ (No. 2) of Fig. 1. As shown in the inset of Fig. 2, $(C_{11}-C_{12})/2$ at low temperatures exhibits a shoulder-like anomaly around 200 mK and shows no sign of long-range ordering down to 20 mK. The solid line for $(C_{11}-C_{12})/2$ in Fig. 2 is a fit in terms of the multipole susceptibility including both quadrupole and hexadecapole with $\Gamma_{3g}$ representation to reproduce the minimum around 28 K corresponding to half of the first $\Gamma_4$ excited energy $\varDelta = 56$ K. Details are shown in the following section.

### B. Analysis by multipole susceptibility

We analyze the temperature dependence of the elastic constant $(C_{11}-C_{12})/2$ for $PrMg_3$ in Fig. 2 in terms of the

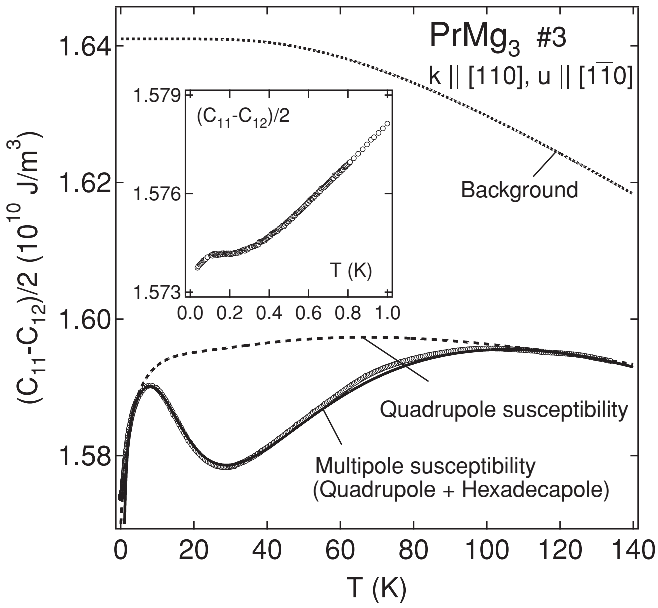


FIG. 2. Elastic constant $(C_{11}-C_{12})/2$ as a function of temperature in $PrMg_3$ (No. 3). The broken line is a theoretical fit by the quadrupole susceptibility with $\lambda = 0$. The solid line is a fit in terms of the multipole susceptibility of both quadrupole and hexadecapole with $\lambda = 0.0135$. The inset shows an enlarged view below 1 K.

multipole susceptibility. The CEF Hamiltonian for the ground $J = 4$ multiplet of the $f^2$ configuration of a $Pr^{3+}$ ion in the cubic point symmetry is written as[5]

$$\mathcal{H}_{\rm CEF} = \sum_{l,m} B_l^m O_l^m = B_4\left(O_4^0 + 5O_4^4\right) + B_6\left(O_6^0 - 21O_6^4\right). \tag{1}$$

Here, $O_l^m$ is the Steven's equivalent operator.[20] The CEF parameters of $B_4 = -3.96 \times 10^{-2}$ K and $B_6 = -1.06 \times 10^{-3}$ K are adopted in accordance with the level scheme of $\Gamma_3$ (0 K)–$\Gamma_4$ (56 K)–$\Gamma_1$ (135 K)–$\Gamma_5$ (183 K) determined by the inelastic neutron scattering on polycrystalline $PrMg_3$.[17] Recently, neutron spectroscopy of a single crystal of $PrMg_3$ has been performed.[21] The resultant CEF level scheme is consistent with the previous reports. The direct product of the $\Gamma_3$ doublet is reduced as a direct sum $\Gamma_3 \otimes \Gamma_3 = \Gamma_{1g} \oplus \Gamma_{2u} \oplus \Gamma_{3g}$. This implies that the $\Gamma_3$ ground state of $PrMg_3$ has two electric quadrupoles $O_u = (2J_z^2 - J_x^2 - J_y^2)/\sqrt{3}$ and $O_v = J_x^2 - J_y^2$ with $\Gamma_{3g}$ representation and the magnetic octupole $T_{xyz} = \sqrt{15}\,\overline{J_xJ_yJ_z}/6$ with $\Gamma_{2u}$. Here, the bar means the sum of cyclic permutations on $x$, $y$, and $z$. Among them, the electric quadrupole $O_v$ couples to the elastic strain $\varepsilon_v = \varepsilon_{xx} - \varepsilon_{yy}$ associated with the transverse $(C_{11}-C_{12})/2$ with $\boldsymbol{k} \parallel [110]$ and $\boldsymbol{u} \parallel [1\bar{1}0]$ in the experiment. It is expected that the present $PrMg_3$ system with the $\Gamma_3$ doublet–$\Gamma_4$ triplet states possesses $5^2 = 25$ multipoles, because the direct product of the quasi-quintet is reduced as $(\Gamma_3 \oplus \Gamma_4) \otimes (\Gamma_3 \oplus \Gamma_4) = 2\Gamma_{1g} \oplus \Gamma_{2u} \oplus 2\Gamma_{3g} \oplus 2\Gamma_{4u} \oplus \Gamma_{4g} \oplus 2\Gamma_{5g} \oplus \Gamma_{5u}$. It should be noted that the hexadecapoles $H_u$ and $H_v$ and the quadruples $O_u$ and $O_v$ with $\Gamma_{3g}$ are relevant to the present $\Gamma_3$-$\Gamma_4$ system. Therefore, the coupling Hamiltonian of the elastic strain $\varepsilon_v$ of the transverse $(C_{11}-C_{12})/2$ mode to an electric multipole $\tilde{O}_v$ with $\Gamma_{3g}$, which is expressed by a linear combination of the quadrupole $O_v$ and the hexadecapole $H_v$, is written as

$$\mathcal{H}_{MS} = -g_{\Gamma 3}\tilde{O}_v\varepsilon_v = -g_{\Gamma 3}(O_v + \lambda H_v)\varepsilon_v. \tag{2}$$

Here, $g_{\Gamma 3}$ is a coupling constant and $\lambda$ is the contribution ratio of the hexadecapole to the quadrupole. The hexadecapole $H_v$ is written as[22]

$$H_v = \tfrac{1}{4}\{[7J_z^2 - J(J+1) - 5](J_+^2 + J_-^2) + (J_+^2 + J_-^2)[7J_z^2 - J(J+1) - 5]\}. \tag{3}$$

Here, $J_\pm = J_x \pm iJ_y$ are ladder operators. In Fig. 3, we show schematic views of the anisotropic charge distribution of the quadrupole $O_v$ and the hexadecapole $H_v$.

The important role of the hexadecapole for the elastic properties of cubic PrSb with the $\Gamma_1$ singlet–$\Gamma_4$ triplet states (Ref. 23) and that of hexagonal $PrNi_5$ (Ref. 24) was previously discussed. Furthermore, the significance of the hexadecapole in the filled skutterudite $PrOs_4Sb_{12}$ with singlet-triplet states was also studied theoretically.[25] The hexadecapole may commonly play a significant role for the elastic properties, particularly in the Pr-based compounds with multiple degenerate states.

The softening of the present $PrMg_3$ is affected by the intersite interaction due to the electric multipole $\tilde{O}_v = O_v + \lambda H_v$. This mutipole intersite interaction in unit volume is explained as

$$\mathcal{H}_{MM} = -\sum_{i>j} G_{\Gamma 3}^{ij}\tilde{O}_v(i)\tilde{O}_v(j) = -g'_{\Gamma 3}\sum_i \langle\tilde{O}_v\rangle\tilde{O}_v(i). \tag{4}$$

Here, $g'_{\Gamma 3}$ is the coupling constant of intersite multipole interactions in the mean-field approximation as $g'_{\Gamma 3} = zG_{\Gamma 3}^{ij}$ for an effective neighbor-site number $z$. The temperature dependence of the elastic constant $C_{\Gamma 3} = (C_{11}-C_{12})/2$ can be written as[26]

$$C_{\Gamma 3}(T) = C_{\Gamma 3}^0 - \frac{Ng_{\Gamma 3}^2\chi_{\Gamma 3}(T)}{1 - g'_{\Gamma 3}\chi_{\Gamma 3}(T)}. \tag{5}$$

Here, $C_{\Gamma 3}^0$ denotes a background of the elastic constant and $N$ is the number of Pr ions per unit volume. The multipole susceptibility of $\chi_{\Gamma 3}(T)$ is written as

$$-g_{\Gamma 3}^2\chi_{\Gamma 3}(T) = \left\langle\frac{\partial^2 E_i}{\partial\varepsilon_v^2}\right\rangle - \frac{1}{k_BT}\left\{\left\langle\left(\frac{\partial E_i}{\partial\varepsilon_v}\right)^2\right\rangle - \left\langle\frac{\partial E_i}{\partial\varepsilon_v}\right\rangle^2\right\}. \tag{6}$$

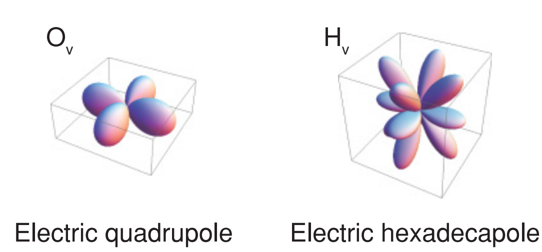


FIG. 3. (Color online) Charge distribution of the quadrupole $O_v$ and the hexadecapole $H_v$ with $\Gamma_{3g}$ representation.

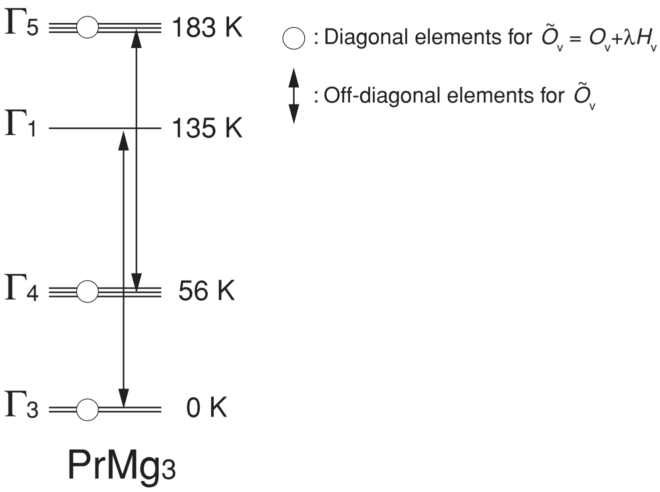


FIG. 4. CEF level scheme for the $Pr^{3+}$ ion of $PrMg_3$ in point-group symmetry $O_h$. Circles and arrows represent selection rules of transitions for the electric multipole moment $\tilde{O}_v$ including the quadrupole $O_v$ and the hexadecapole $H_v$ with $\Gamma_{3g}$ representation of Eq. (2) in the text.

Here, $\langle A\rangle$ denotes a thermal average for a physical quantity $A$ for the CEF levels. $E_i$ is second-order perturbation energy with respect to the elastic strain $\varepsilon_{\Gamma 3} = \varepsilon_v$ for the CEF state of $PrMg_3$. The first part on the right-hand side is the van Vleck term corresponding to off-diagonal transitions, while the second part is a Curie term due to diagonal elements. The Curie term leads to sizable softening proportional to the reciprocal temperature and the van Vleck term behaves in an almost temperature independent manner at low temperatures. In the present $PrMg_3$, the Curie terms of the $\Gamma_3$ ground state and the $\Gamma_4$ excited state dominate the multipole susceptibility $\chi_{\Gamma 3}$ in the vicinity of the characteristic minimum around 28 K of the $(C_{11}-C_{12})/2$ as shown in Fig. 4. The elastic softening in various rare-earth compounds is usually described in terms of the quadrupole susceptibility only considering the quadrupole-strain interaction. The fitting of the susceptibility in a framework of conventional quadrupole-strain interaction with $\lambda = 0$ in Eq. (2) for $(C_{11}-C_{12})/2$ of $PrMg_3$ is represented by a broken line in Fig. 2. This fitting succeeded well in explaining of the softening in $(C_{11}-C_{12})/2$ below 8 K, but it is rather difficult to reproduce the characteristic minimum in $(C_{11}-C_{12})/2$ around 28 K.

TABLE I. Parameters in fitting for the elastic constant $(C_{11}-C_{12})/2$ of Pr-based $\Gamma_3$-$\Gamma_4$ systems of $PrMg_3$, $PrAg_2In$, and $PrPb_3$ using multipole susceptibility with $\lambda \neq 0$ of Eq. (6).

| Samples<br>Samples | Multipole-Strain<br>Interaction $\lvert g_{\Gamma 3}\rvert$ | Contribution<br>Ratio $\lambda$ | Intersite<br>Interaction $g'_{\Gamma 3}$ |
|---|---|---|---|
| $PrMg_3$ (No. 3) | 48.5 K | 0.0135 | −6 mK |
| $PrAg_2In$ | 27 K | 0.0133 | −4 mK |
| $PrPb_3$ | 45 K | 0.0076 | −10 mK |

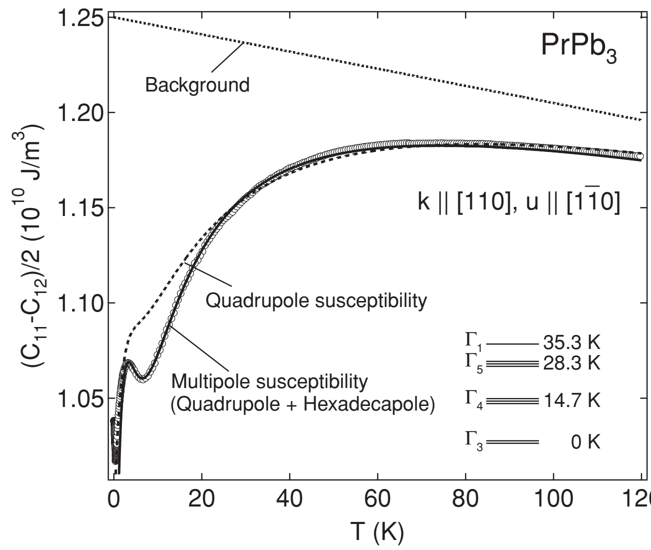


FIG. 5. Elastic constant $(C_{11}-C_{12})/2$ of $PrPb_3$ as a function of temperature (Ref. 28). The broken line is a fit based on the quadrupole susceptibility with $\lambda = 0$. The solid line is a fit in terms of the multipole susceptibility of both the quadrupole and hexadecapole with $\lambda = 0.0076$ in Eq. (2). The dotted line shows the background for the multipole susceptibility of Eq. (6) for $(C_{11}-C_{12})/2$.

The multipole susceptibility for the multipole-strain interaction of Eq. (2), where both the quadrupole and hexadecapole are included, successfully explains the minimum around 28 K in $(C_{11}-C_{12})/2$. The solid line in Fig. 2 is a fit with the multipole susceptibility with parameters of $|g_{\Gamma 3}| = 48.5$ K, $\lambda = 0.0135$, and $g'_{\Gamma 3} = -6$ mK for $PrMg_3$ (No. 3). The negative sign of $g'_{\Gamma 3}$ indicates the antiferro-type multipole intersite interaction in the present $PrMg_3$ system. In Table I, we summarize the fitting parameters of $PrMg_3$ (No. 3) together with results of $PrAg_2In$ and $PrPb_3$, as will be mentioned later.

### C. Comparison with other Pr-based $\Gamma_3$-$\Gamma_4$ systems

It is worthwhile to discuss a common feature of the multipole effects across the Pr-based $\Gamma_3$-$\Gamma_4$ systems of the present $PrMg_3$, $PrPb_3$, and $PrAg_2In$. It was reported by Niksch *et al.*[14] that $PrPb_3$ with the $\Gamma_3$ doublet ground state and the $\Gamma_4$ triplet excited state located at 14.7 K (Ref. 27) reveals the minimum around 7 K in the elastic constant $(C_{11}-C_{12})/2$. They already pointed out that the multipole susceptibility including both the quadrupole and hexadecapole reproduces well the characteristic minimum of $(C_{11}-C_{12})/2$. Furthermore, the other Pr-based $\Gamma_3$-$\Gamma_4$ system of $PrAg_2In$ also exhibits the minimum in $(C_{11}-C_{12})/2$ around 35 K.[6] In Fig. 5, we present the fitting for $PrPb_3$ indicated by the solid line based on the multipole susceptibility with parameters of $|g_{\Gamma 3}| = 45$ K, $\lambda = 0.0076$, and $g'_{\Gamma 3} = -10$ mK. Here, we use ultrasonic results of $PrPb_3$ in our group.[28] The result shows essentially the same behavior as in Ref. 14. The CEF level scheme of $PrPb_3$ in Fig. 5 is derived from Ref. 27. The minimum around 7 K in $(C_{11}-C_{12})/2$ of $PrPb_3$ corresponds mostly to half of the excited energy $\Delta = 14.7$ K of the $\Gamma_4$ triplet state.

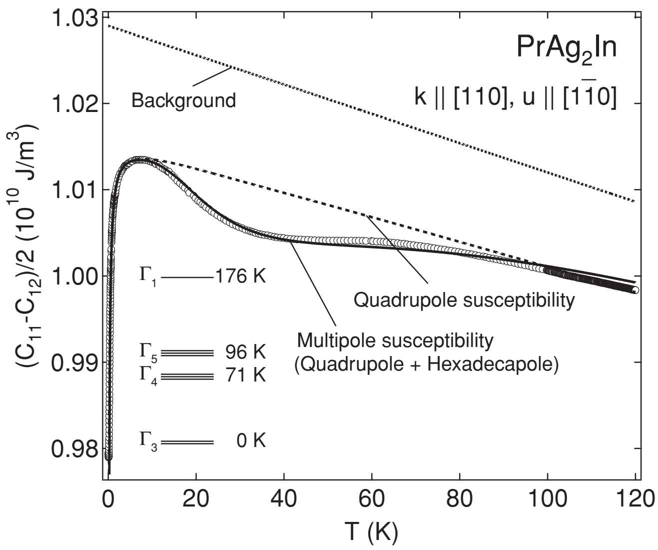


FIG. 6. Elastic constant $(C_{11}-C_{12})/2$ as a function of temperature (Ref. 6) of $PrAg_2In$. The broken line is a fit based on the quadrupole susceptibility with $\lambda = 0$. The solid line is a fit in terms of the multipole susceptibility of both quadrupole and hexadecapole with $\lambda = 0.0133$. The dotted line shows the background for the multipole susceptibility of Eq. (6) for $(C_{11}-C_{12})/2$.

The characteristic minimum around 35 K in $(C_{11}-C_{12})/2$ of $PrAg_2In$ in Fig. 6 of Ref. 6 is also well reproduced by the solid line of the multipole susceptibility with $|g_{\Gamma 3}| = 27$ K, $\lambda = 0.0133$, and $g'_{\Gamma 3} = -4$ mK. The CEF levels of $PrAg_2In$ in our Fig. 6 is derived from the results of neutron scatterings in Ref. 29. This minimum in $(C_{11}-C_{12})/2$ of $PrAg_2In$, as well as in the cases of $PrPb_3$ and the present $PrMg_3$, corresponds to half of the splitting energy $\Delta = 71$ K of the $\Gamma_4$ triplet exited state.

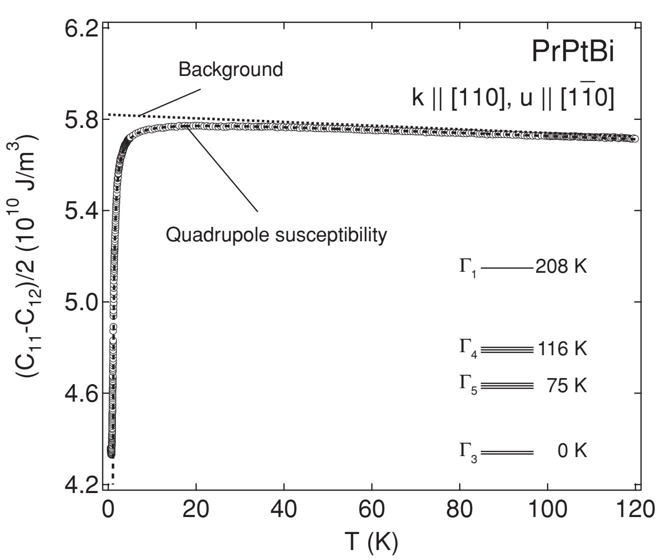


FIG. 7. Elastic constant $(C_{11}-C_{12})/2$ as a function of temperature for PrPtBi (Ref. 30). The broken and dotted lines show a fit by quadrupole susceptibility with $\lambda = 0$ and the background of $(C_{11}-C_{12})/2$, respectively.

On the other hand, it is notable that $(C_{11}-C_{12})/2$ of PrPtBi with the $\Gamma_3$ ground state and the first excited $\Gamma_5$ triplet state located at 75 K shows no apparent minimum as shown in Fig. 7 in Ref. 30. The broken line in our Fig. 7 by a fit in terms of the quadrupole susceptibility with $|g_{\Gamma 3}| = 30$ K, $\lambda = 0$, and $g'_{\Gamma 3} =$ 38 mK reproduces the experimental result of PrPtBi. Here, we used the CEF levels of Fig. 7 in Ref. 10. According to the group theoretical viewpoint, the quasi-quintet of $\Gamma_3 \oplus \Gamma_5$ possesses the quadrupole and the hexadecapole with $\Gamma_{3g}$ representation as well. The $(C_{11}-C_{12})/2$ of PrPtBi with $\Gamma_3$-$\Gamma_5$ states shows no obvious minimum, which is markedly different from the minimum of $(C_{11}-C_{12})/2$ of $PrMg_3$, $PrPb_3$, and $PrAg_2In$ with $\Gamma_3$-$\Gamma_4$ states.

It is worthwhile to compare the elastic softening for the $\Gamma_3$-$\Gamma_4$ system in Fig. 8(a) and that for the $\Gamma_3$-$\Gamma_5$ in Fig. 8(b) by using the multipole susceptibility as

$$-\chi^{(3,i)}_{\Gamma 3}\Delta = -\frac{2\Delta}{k_B T Z}\Big[\langle\Gamma_3|\tilde{O}_v|\Gamma_3\rangle^2 + \langle\Gamma_i|\tilde{O}_v|\Gamma_i\rangle^2 \times \exp\Big(-\frac{\Delta}{k_B T}\Big)\Big] \quad (i = 4 \text{ or } 5), \qquad (7)$$

where $Z$ is the partition function for the corresponding levels. We consider only low-lying states of the $\Gamma_3$ doublet ground state and the $\Gamma_4$ or $\Gamma_5$ triplet excited state located at $\Delta$ K for simplicity. We adopt the same ratio $\lambda = 0.01$ for both calculations to examine the contribution of the hexadecapole to the appearance of the minimum in the temperature dependence

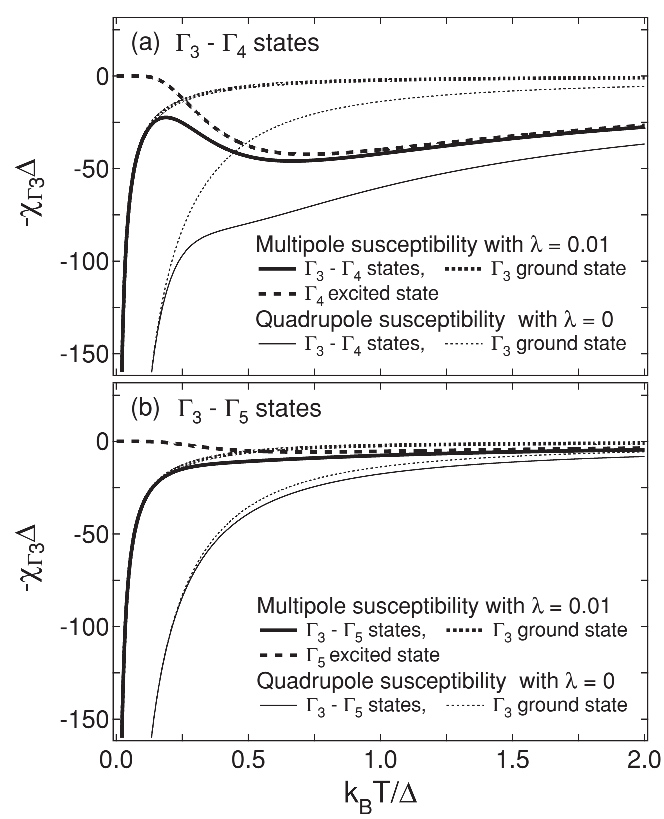


FIG. 8. Temperature dependence of the multipole susceptibilities of Eq. (7) in the text with $\lambda = 0.01$ in $(C_{11}-C_{12})/2$ for the systems with $\Gamma_3$ doublet–$\Gamma_4$ triplet states in (a) and $\Gamma_3$ doublet–$\Gamma_5$ triplet states in (b).

of $(C_{11}-C_{12})/2$. The matrix elements for both the quadrupole $O_v$ and hexadecapole $H_v$ of $Pr^{3+}$ ($J = 4$) ion in the cubic symmetry are presented in the Appendix.

It should be noted that the multipole susceptibility for the Curie term of the $\Gamma_4$ excited state with $\langle\Gamma_4^\alpha|\tilde{O}_v|\Gamma_4^\alpha\rangle = 12.95$, $\langle\Gamma_4^\beta|\tilde{O}_v|\Gamma_4^\beta\rangle = 0$, and $\langle\Gamma_4^\gamma|\tilde{O}_v|\Gamma_4^\gamma\rangle = -12.95$, shown by a thick broken line in Fig. 8(a), indicates the significant minimum around $\Delta/2$ K corresponding to that of the experimental results of $(C_{11}-C_{12})/2$ in $PrMg_3$, $PrPb_3$, and $PrAg_2In$ with $\Gamma_3$-$\Gamma_4$ states. Such behavior possessing the minimum is also seen in the quadrupole susceptibility due to the $\Gamma_4$ excited state with $\langle\Gamma_4^\alpha|O_v|\Gamma_4^\alpha\rangle = 14$, $\langle\Gamma_4^\beta|O_v|\Gamma_4^\beta\rangle = 0$, and $\langle\Gamma_4^\gamma|O_v|\Gamma_4^\gamma\rangle = -14$ (not shown here). However, the quadrupole susceptibility for $\Gamma_3$-$\Gamma_4$ states shows only a weak shoulder around $\Delta/2$ K as represented by a thin solid line in Fig. 8(a), because the elastic softening due to the $\Gamma_3$ ground state with $\langle\Gamma_3^\alpha|O_v|\Gamma_3^\alpha\rangle = 8/\sqrt{3}$ and $\langle\Gamma_3^\beta|O_v|\Gamma_3^\beta\rangle = -8/\sqrt{3}$ is dominant at low temperatures as shown by a thin dotted line in Fig. 8(a).

When we take account of the hexadecapole in addition to the quadrupole, the multipole susceptibility for $\Gamma_3$-$\Gamma_4$ states shows a clear minimum as shown by a thick solid line in Fig. 8(a). This occurs because the susceptibility for the Curie term of the $\Gamma_3$ doublet with $\langle\Gamma_3^\alpha|\tilde{O}_v|\Gamma_3^\alpha\rangle = 3.2/\sqrt{3}$ and $\langle\Gamma_3^\beta|\tilde{O}_v|\Gamma_3^\beta\rangle = -3.2/\sqrt{3}$ as shown by a thick dotted line reveals shifting to lower temperatures compared to that for the Curie term with $\langle\Gamma_3^\alpha|O_v|\Gamma_3^\alpha\rangle$ and $\langle\Gamma_3^\beta|O_v|\Gamma_3^\beta\rangle$ as shown by the thin dotted line in Fig. 8(a).

Furthermore, the Curie term due to the $\Gamma_5$ excited triplet with $\langle\Gamma_5^\alpha|\tilde{O}_v|\Gamma_5^\alpha\rangle = 4.75$, $\langle\Gamma_5^\beta|\tilde{O}_v|\Gamma_5^\beta\rangle = 0$, and $\langle\Gamma_5^\gamma|\tilde{O}_v|\Gamma_5^\gamma\rangle = -4.75$ makes a relatively small contribution in comparison with that due to the $\Gamma_4$ excited triplet. Consequently, the minimum in the temperature dependence of $(C_{11}-C_{12})/2$ is expected to emerge in the $\Gamma_3$-$\Gamma_4$ system, but is irrelevant for the $\Gamma_3$-$\Gamma_5$ system.

## IV. SUMMARY

In the present study, we have performed ultrasonic measurements of the Pr-based compound $PrMg_3$ with the $\Gamma_3$ doublet ground state and $\Gamma_4$ triplet first excited state located at 54 K. The characteristic minimum around 28 K and pronounced softening below 8 K are observed in the transverse elastic constant $(C_{11}-C_{12})/2$. The multipole susceptibility including the hexadecapole $H_v$ as well as the quadrupole $O_v$ with $\Gamma_{3g}$ representation describes well the minimum and the following softening in $(C_{11}-C_{12})/2$. The common feature of the minimum in $(C_{11}-C_{12})/2$ for the pseudo-quintet $\Gamma_3$-$\Gamma_4$ systems of $PrMg_3$ in the present experiments and $PrPb_3$ and $PrAg_2In$ in previous research arises from the multipole susceptibility. In contrast, the $(C_{11}-C_{12})/2$ of PrPtBi with the $\Gamma_3$ ground state and the $\Gamma_5$ triplet first excited state shows no apparent minimum, because the matrix elements of $\tilde{O}_v = O_v + \lambda H_v$ for the $\Gamma_5$ state are smaller than those of the $\Gamma_4$ state. The higher rank hexadecapole, as well as the quadrupole, plays a significant role in the elastic properties of the Pr-based $\Gamma_3$-$\Gamma_4$ multiply degenerated systems.

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## APPENDIX: MATRIX ELEMENTS FOR THE QUADRUPOLE $O_v$ AND HEXADECAPOLE $H_v$

This Appendix gives matrix elements for the quadrupole $O_v$ and the hexadecapole $H_v$ of the $Pr^{3+}$ ($J = 4$) ion in the cubic point symmetry. The eigenstates for $J = 4$ of $Pr^{3+}$ ion in the cubic system are chosen to be diagonal for $H_{CEF}$ of Eq. (1) in Ref. 5. In the present paper, however, we adopt alternative eigenstates for the diagonal matrices of the quadrupole $O_v$ and hexadecapole $H_v$ of Eq. (3).

$$O_v = \begin{array}{c} \langle\Gamma_1| \\ \langle\Gamma_3^\alpha| \\ \langle\Gamma_3^\beta| \\ \langle\Gamma_4^\alpha| \\ \langle\Gamma_4^\beta| \\ \langle\Gamma_4^\gamma| \\ \langle\Gamma_5^\alpha| \\ \langle\Gamma_5^\beta| \\ \langle\Gamma_5^\gamma| \end{array} \overset{\begin{array}{ccccccccc} |\Gamma_1\rangle & |\Gamma_3^\alpha\rangle & |\Gamma_3^\beta\rangle & |\Gamma_4^\alpha\rangle & |\Gamma_4^\beta\rangle & |\Gamma_4^\gamma\rangle & |\Gamma_5^\alpha\rangle & |\Gamma_5^\beta\rangle & |\Gamma_5^\gamma\rangle \end{array}}{\begin{pmatrix} 0 & 4\sqrt{\frac{35}{6}} & -4\sqrt{\frac{35}{6}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 4\sqrt{\frac{35}{6}} & \frac{8}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -4\sqrt{\frac{35}{6}} & 0 & -\frac{8}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 14 & 0 & 0 & 0 & 0 & \sqrt{7} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\sqrt{7} & 0 \\ 0 & 0 & 0 & 0 & 0 & -14 & -\sqrt{7} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{7} & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{7} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{7} & 0 & 0 & 0 & 0 & -4 \end{pmatrix}}, \qquad (A1)$$

$$H_v = \begin{array}{c} \\ \langle\Gamma_1| \\ \langle\Gamma_3^\alpha| \\ \langle\Gamma_3^\beta| \\ \langle\Gamma_4^\alpha| \\ \langle\Gamma_4^\beta| \\ \langle\Gamma_4^\gamma| \\ \langle\Gamma_5^\alpha| \\ \langle\Gamma_5^\beta| \\ \langle\Gamma_5^\gamma| \end{array} \begin{array}{c} \begin{array}{ccccccccc} |\Gamma_1\rangle & |\Gamma_3^\alpha\rangle & |\Gamma_3^\beta\rangle & |\Gamma_4^\alpha\rangle & |\Gamma_4^\beta\rangle & |\Gamma_4^\gamma\rangle & |\Gamma_5^\alpha\rangle & |\Gamma_5^\beta\rangle & |\Gamma_5^\gamma\rangle \end{array} \\ \begin{pmatrix} 0 & 12\sqrt{\frac{35}{6}} & -12\sqrt{\frac{35}{6}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 12\sqrt{\frac{35}{6}} & -160\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -12\sqrt{\frac{35}{6}} & 0 & 160\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -105 & 0 & 0 & 0 & 0 & 45\sqrt{7} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 90\sqrt{7} & 0 \\ 0 & 0 & 0 & 0 & 0 & 105 & -45\sqrt{7} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -45\sqrt{7} & 75 & 0 & 0 \\ 0 & 0 & 0 & 0 & 90\sqrt{7} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 45\sqrt{7} & 0 & 0 & 0 & 0 & -75 \end{pmatrix} \end{array}, \qquad \text{(A2)}$$

$$\begin{aligned}
|\Gamma_1\rangle &= \sqrt{\frac{5}{24}}(|+4\rangle + |-4\rangle) + \sqrt{\frac{7}{12}}|0\rangle, \\
|\Gamma_3^\alpha\rangle &= -\sqrt{\frac{7}{48}}(|+4\rangle + |-4\rangle) + \frac{1}{2}(|+2\rangle + |-2\rangle) + \sqrt{\frac{5}{24}}|0\rangle, \\
|\Gamma_3^\beta\rangle &= -\sqrt{\frac{7}{48}}(|+4\rangle + |-4\rangle) - \frac{1}{2}(|+2\rangle + |-2\rangle) + \sqrt{\frac{5}{24}}|0\rangle, \\
|\Gamma_4^\alpha\rangle &= -\frac{1}{4}(|+3\rangle + |-3\rangle) - \frac{\sqrt{7}}{4}(|+1\rangle + |-1\rangle), \\
|\Gamma_4^\beta\rangle &= \sqrt{\frac{1}{2}}(|+4\rangle - |-4\rangle), \\
|\Gamma_4^\gamma\rangle &= \frac{1}{4}(|+3\rangle - |-3\rangle) - \frac{\sqrt{7}}{4}(|+1\rangle - |-1\rangle), \\
|\Gamma_5^\alpha\rangle &= \frac{\sqrt{7}}{4}(|+3\rangle - |-3\rangle) + \frac{1}{4}(|+1\rangle - |-1\rangle), \\
|\Gamma_5^\beta\rangle &= \sqrt{\frac{1}{2}}(|+2\rangle - |-2\rangle), \\
|\Gamma_5^\gamma\rangle &= -\frac{\sqrt{7}}{4}(|+3\rangle + |-3\rangle) + \frac{1}{4}(|+1\rangle + |-1\rangle).
\end{aligned} \qquad \text{(A3)}$$

Here, $|J_z\rangle$ of Eq. (A3) denotes the eigenket for the $z$ component of total angular momentum $J = 4$.

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