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# Ultrasonic dispersion due to off-center rattling in $NdOs_4Sb_{12}$

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**Abstract**

Ultrasonic investigation for the single crystals of ferromagnetic filled skutterudite compound $NdOs_4Sb_{12}$ was performed. A marked frequency dependence of the ultrasonic dispersion has been observed in a longitudinal elastic constant $C_{11}$ at temperature centered around 45 K; however, no dispersion was measured in the transverse elastic constant $C_{44}$. Such a clear mode difference in the ultrasonic dispersion, which has been found in $PrOs_4Sb_{12}$, strongly suggests that Nd ion in $NdOs_4Sb_{12}$ bears thermally activated off-center rattling effect.


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*Keywords:* Filled skutterudite; $NdOs_4Sb_{12}$; Rattling; Elastic constant; Ultrasonic dispersion

## 1. Introduction

The lanthanide filled skutterudite compound with the formula $RT_4X_{12}$ (R = lanthanide; T = Fe, Ru, or Os; X = P, As, or Sb) is an ideal system to study the off-center rattling motion of a guest atom in an oversized atomic cage (shown in Fig. 1). This class of compounds has recently attracted a great deal of attention of not only as potential materials for use in thermoelectric devices but also because they exhibit a variety of strongly correlated electron phenomena. [1] Since the off-center rattling phenomenon has been found in the unconventional superconductor $PrOs_4Sb_{12}$ [2,3] and other clathrate compounds $R_3Pd_{20}Ge_6$ ($R = lanthanide$) by ultrasonic measurements [4,5], it has recently been recognized that the strong coupling between conduction electrons and local atomic vibrations in these systems induce charge fluctuations, which may give rise to strongly correlated electron phenomena such as heavy fermion behavior at low temperatures [6,7]. Several experimental approaches other than ultrasound, such as neutron, Raman scattering, NMR and NQR have also been taken to study rattling behavior [8]. Most recently, NMR measurements have revealed anomalous negative hyperfine coupling constants in $LaOs_4Sb_{12}$, $LaFe_4Sb_{12}$ and $LaOs_4P_{12}$, which display rattling effect, while the other compounds typically show positive hyperfine coupling constants [9]. These results suggest that the electron–phonon coupling between the conduction band of the transition metal ions and the rattling motion may play an important role in the observability of rattling in ultrasound.

In order to seek other evidence of off-center rattling phenomena, ultrasonic investigations of the filled skutterudite $NdOs_4Sb_{12}$ were performed. The compound $NdOs_4Sb_{12}$ becomes ferromagnetic below 0.9 K. An enhanced electronic specific heat coefficient $\gamma \sim 520\,\mathrm{mJ/mol\,K^2}$ was estimated from specific heat measurements, which suggests the existence of an anomalous interaction between the Nd 4f- and conduction electrons in this compound [11]. The crystalline electric field ground state has been determined as the $\Gamma_{67}^{(2)}$ quartet in $T_h$ symmetry, since low temperature softening of the elastic constant $C_{44}$ mode ($k\|[0\,0\,1], u\|[1\,0\,0]$) was found in a previous ultrasonic study [10]. In this work, further

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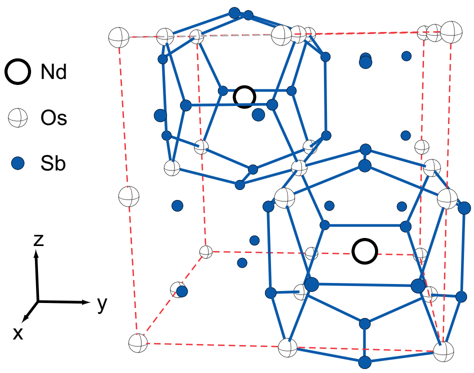


Fig. 1. Crystal structure of the filled skutterudite $NdOs_4Sb_{12}$, in which the $(OsSb_3)_4$ cages are emphasized.

ultrasonic measurements in the $C_{11}$ mode ($k\|u\|[0\,0\,1]$) were performed.

## 2. Experimental details

Single crystals of $NdOs_4Sb_{12}$ were grown by the metallic flux growth method [12]. No significant impurity phases were detected in any of the samples except for small quantities of free Sb. Two single crystals with dimensions of $2.00 \times 0.75 \times 0.50$ mm (Sample#1) and $1.00 \times 0.50 \times 0.50$ mm (Sample#2), both of which were selected from different sample batches, were used in the present measurements in order to check the reproducibility. Sound velocity $v$ was measured by phase comparative method. $LiNbO_3$ transducers bonded onto the sample surfaces were used for generation and detection of ultrasonic waves. $^3$He refrigerator with superconducting magnet to temperatures down to 400 mK and magnetic fields up to 12 T was used for present ultrasonic measurements. The elastic constant $C_{11} = 17.56\,\mathrm{J/m^3}$ and $C_{44} = 3.198\,\mathrm{J/m^3}$ at 80 K were estimated by $C_{ij} = \rho v_{ij}^2$ with the mass density $\rho = 9.7467\,\mathrm{g/cm^3}$ and lattice constant $a = 0.93075(2)$ nm of $NdOs_4Sb_{12}$.

## 3. Results and discussions

Fig. 2 shows relative change of the elastic constants $C_{11}$ (upper) and $C_{44}$ (lower) as a function of temperature in $NdOs_4Sb_{12}$ from the present work and $PrOs_4Sb_{12}$, taken from Ref. [13], for comparison. Both sets of data show low temperature softening below 10 K. The $C_{11}$ has a clear upturn around 40 K; on the other hand, the $T$-dependence of the $C_{44}$ mode exhibit monotonic change. In the case of $PrOs_4Sb_{12}$, the $\Gamma_{23}$ related elastic constant $(C_{11}-C_{12})/2$ also shows such a similar upturn (not shown) [2], and displays an ultrasonic dispersion accompanied by ultrasonic attenuation. Since the findings in $PrOs_4Sb_{12}$, such feature in $\Gamma_{23}$-related elastic constant are considered as evidence for its coupling to the off-center rattling mode of the rare-earth ion.

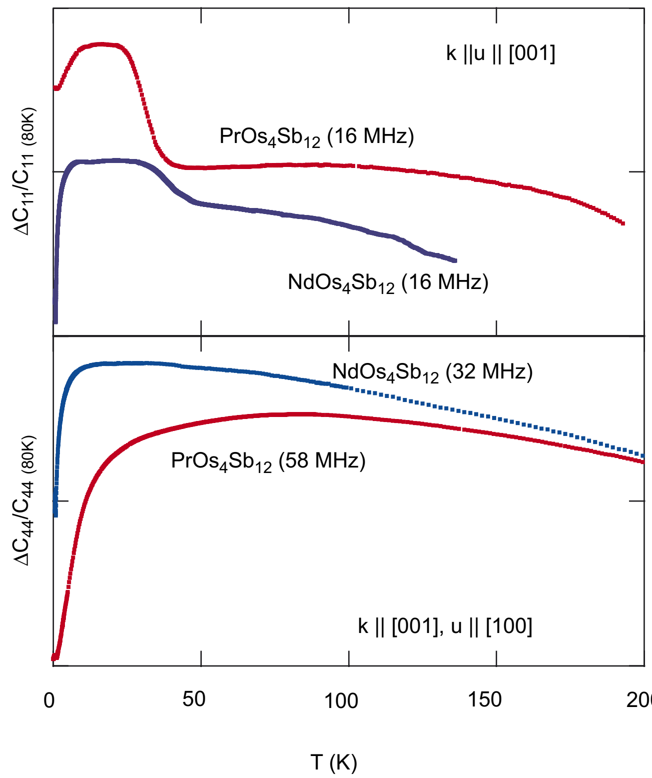


Fig. 2. Comparison of the relative change of elastic constants $C_{11}$ and $C_{44}$ in $NdOs_4Sb_{12}$ and $PrOs_4Sb_{12}$ [12] as a function of temperature.

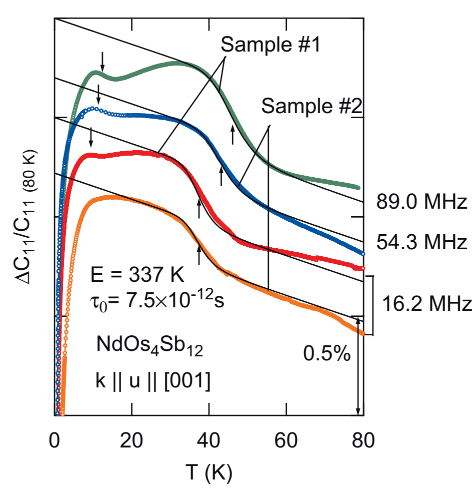


Fig. 3. Ultrasonic dispersion in the elastic constant $C_{11}$ vs. temperature of $NdOs_4Sb_{12}$ with frequencies of 16.2, 54.3 and 89.0 MHz. Data for samples #1 and #2 are compared shifted vertically 0.2% for easy viewability. Upper arrows indicate the temperatures where the system attains the resonance conditions $\omega\tau \sim 1$. Lower arrows indicate elastic anomalies, which were found around 10 K. Solid lines show theoretical fits.

In order to examine the ultrasonic dispersion appearing in the $C_{11}$ mode, the frequency dependence of the elastic constant $C_{11}$ was measured for two single crystals of $NdOs_4Sb_{12}$. Fig. 3 shows the relative change of $C_{11}$ as a function of temperature at several ultrasonic frequencies. The data are offset by 0.2% for clarity. Both samples #1 and #2 show good reproducibility. The upturn around