Ultrasound measurements in the spinel compound
GeCo$_2$O$_4$

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Abstract. Elastic properties of the spinel compound GeCo$_2$O$_4$ were investigated by the ultrasound velocity measurements in the single crystal. Absence of the elastic softening in $(C_{11} - C_{12})/2$ in the paramagnetic state suggests the Jahn-Teller inactive character of Co$^{2+}$, despite the presence of the orbital degree of freedom. The pronounced $C_{44}$ anomaly in the paramagnetic state near $T_N$ alternatively suggests that the ultrasound dominantly couple to the exchange interactions among Co$^{2+}$ ions by the exchange striction effect. The present results conclude that Co$^{2+}$ adopts the high spin state in this substance. In the antiferromagnetic phase, new elastic anomalies were observed only in $(C_{11} - C_{12})/2$ implying the occurrence of the magnetic transitions triggered by the exchange interactions within the Co$^{2+}$ bonds along [110] directions.

1. Introduction
Geometrical frustration in magnets has recently been an active topic in the condensed matter physics because of the variety of the intriguing quantum phenomena such as spin ice, spin liquid, and heavy-fermionic behavior [1]. Two-dimensional triangular lattice and kagome lattice with the antiferromagnetic (AF) exchange interactions are the most simple frame for the geometrical frustration. Pyrochlore lattice has been focused as a three-dimensional stage for the geometrical frustration which is more realistic for the experimental studies. In this system, the magnetic ions occupy the vertices of a three-dimensional array of corner sharing tetrahedra. Spinel compound $AB_2$O$_4$ is one of the representative, and has been extensively studied. In $AB_2$O$_4$, $B$-site network forms the pyrochlore lattice.

Germanium-based spinel compound GeCo$_2$O$_4$ consists of magnetic Co$^{2+}$ ($3d^7$) ions on the octahedral $B$ sites with non-magnetic Ge$^{4+}$ ions on the tetrahedral $A$ sites [2]. AF transition occurs at $T_N = 23.0$ K accompanied with cubic-to-tetragonal structural transition. The Curie-Weiss temperature, nevertheless, is positive $\Theta_{CW} = 81.0$ K indicating the dominant contribution of the ferromagnetic (FM) interactions. Recent results of neutron powder diffraction suggest, despite the small frustration factor of $f = |T_N/\Theta_{CW}| \simeq 3.5$, the presence of a new frustration due to the competition among several FM and AF interactions even in the AF state [3].

We performed ultrasound velocity measurements in GeCo$_2$O$_4$ single crystal to investigate the elastic properties. Ultrasound is a powerful tool for the study of the orbital degree of freedom and the magnetic phase transition, because ultrasound can sensitively couple to the magnetic...
ions by the strain modulation [4]. We discuss the nature of the magnetism in GeCo$_2$O$_4$ based on our experimental results.

2. Experimental procedure

Large single crystals of GeCo$_2$O$_4$ were grown by the floating zone method [5]. The Néel temperature $T_N$ and the Curie-Weiss temperature $\Theta_{CW}$ determined by the magnetic susceptibility are $T_N = 20.8$ K and $\Theta_{CW} = 12.0$ K, respectively. For the ultrasound measurements, we used a crystal cut into the cuboid shape with the dimension of $3.6 \times 3.5 \times 2.6$ mm$^3$. The ultrasound velocities were measured by the phase comparison method in which the relative change of the sound velocities are measurable within the high precision of $10^{-7}$. For the generation and the detection of the ultrasound, we used the LiNbO$_3$ transducers with the fundamental frequency of 30 MHz. Mirror surfaces of the sample were prepared by careful polishing using the 1$\mu$m diamond slurry, because the ultrasound measurements are quite sensitive to the roughness of the sample surface. The transducers were glued on the parallel surfaces of the sample by the silicone adhesive. In the crystal structure with the cubic symmetry, there are three symmetrically independent elastic constants; $C_{11}$, $C_{12}$, and $C_{44}$. We measured transverse ultrasound velocities in two different combinations of the propagation $k$ and the polarization $u$: $k\parallel[001]$ and $u\parallel[110]$ corresponding to $C_{44}$, and $k\parallel[110]$ and $u\parallel[\bar{1}10]$ corresponding to $(C_{11}-C_{12})/2$. Ultrasound velocities were measured in the temperature from 2 K to 100 K, and the magnetic field from 0 to 7 T.

3. Results and Discussion

Figure 1 depicts the temperature dependence of the sound velocities in $C_{44}$ and $(C_{11}-C_{12})/2$ in zero magnetic field. In the paramagnetic state, $C_{44}$ shows steep softening of $\sim 1.5\%$ below $\sim 35$K down to $T_N$ whereas $(C_{11}-C_{12})/2$ shows slight hardening without any anomaly. Both elastic modes reveal discontinuous anomalies at $T_N$ due to the first-order phase transition. Below $T_N$, the detected echo signals of $C_{44}$ are extremely weakened. This would be due to the magnetic domain-wall stress effect in the AF state.

We would like to discuss the elastic anomaly of $C_{44}$ in the paramagnetic state shown in Figure 1. Figure 2(a) depicts the possible spin state of Co$^{2+}$ on the octahedral $B$ site in the spinel structure. Since Co$^{2+}$ consists of 3$d^7$ electrons, low spin ($S = 1/2$) and high spin ($S = 3/2$) states both contain the orbital degree of freedom. The $e_g$ orbit is Jahn-Teller (JT) active in the low spin state, while the $t_{2g}$ orbit in the high spin state. Transverse sound velocities in

![Figure 1. Temperature dependence of the sound velocity in zero field in $C_{44}$ and $(C_{11}-C_{12})/2$.](image-url)
magnets with the JT active character usually show huge softening due to a magneto-elastic interaction arising the deformation of the crystal field [4]. This mechanism predicts, however, the softening of \( \frac{(C_{11}-C_{12})}{2} \) in GeCo\(_2\)O\(_4\) regardless of the high/low spin state. The present results of the pronounced anomaly in \( C_{44} \) while no anomaly in \( \frac{(C_{11}-C_{12})}{2} \) clearly rule out the possible JT active mechanism. The presence of the strong spin-orbit coupling might play an important role on such an unusual JT-inactive character of this substance.

Another possible magneto-elastic coupling is the one acting on the exchange interactions [4]. In this coupling, the exchange striction arises from a modulation of the exchange interaction by ultrasound as follows:

\[
H_{\text{exs}} = \sum_{ij} [J(\delta + u_i - u_j) - J(\delta)] S_i \cdot S_j
\]

Here \( \delta = R_i - R_j \) is the distance between two magnetic ions and \( u_i \) is the displacement vector for the ion \( R_i \). In Co\(^{2+}\) on the octahedral site, as shown in Figure 2(a), only \( e_g \) orbit can contribute
Cubic Tetragonal

Figure 5. Schematic picture of. (a) Crystal field splitting from cubic to tetragonal structure, and (b) Tetragonal distortion of the Co\textsuperscript{2+} pyrochlore lattice with AF transition in GeCo\textsubscript{2}O\textsubscript{4}.

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