Frustration Effects in Spinel Compound GeCo$_2$O$_4$
Studied by Ultrasound Velocity Measurements

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Abstract. Ultrasound velocity measurements of the cubic spinel GeCo$_2$O$_4$ in the single crystal have been performed for the investigations of shear and compression moduli. The shear moduli reveal the absence of Jahn-Teller activity despite the presence of the orbital degeneracy in the Co$^{2+}$ ions. This Jahn-Teller inactivity indicates that the intersite orbital-orbital interaction is much stronger than the Jahn-Teller coupling. The compression moduli reveal that the dominant path of the exchange interactions for the antiferromagnetic transition lies in the [111] direction. This exchange-path anisotropy is consistent with the antiferromagnetic structure with the wave vector $q \parallel [111]$, suggesting the presence of bond frustration among several ferromagnetic and antiferromagnetic interactions. In the JT-inactive condition, the bond frustration can be induced by geometrical orbital frustration of $t_{2g}$-$t_{2g}$ interaction between the Co$^{2+}$ ions which can be realized in the pyrochlore lattice of the high spin Co$^{2+}$ with $t_{2g}$-orbital degeneracy. In GeCo$_2$O$_4$, the tetragonal elongation below $T_N$ releases the orbital frustration by quenching the orbital degeneracy.

1. Introduction
Frustrated magnet system has been a topical subject for more than a decade in condensed matter physics. Experimental and theoretical studies of geometrical spin frustration have revealed the variety of novel ground states such as spin ice and spin liquid states [1]. In addition to the spin degrees of freedom, the orbital degrees of freedom can expand variations of the frustration effect and the exotic ground state. Cubic spinel structure $AB_2$O$_4$ provides a rich field for the orbital physics in the magnetically frustrated network.

Germanium-based spinel compound GeCo$_2$O$_4$ consists of orbital-degenerate magnetic Co$^{2+}$ ($3d^7$) ions on the octahedral $B$ sites with non-magnetic Ge$^{4+}$ ions on the tetrahedral $A$ sites where the $B$-site Co$^{2+}$ ions form the pyrochlore lattice. In this compound, antiferromagnetic (AF) transition at the Néel temperature $T_N = 23.0$ K occurs accompanied with cubic-to-tetragonal structural elongation [2]. Magnetic susceptibility in the paramagnetic state, on the other hand, exhibits Curie-Weiss behavior with the positive Weiss temperature $\Theta_W = 81.0$ K indicating the dominant contribution of the ferromagnetic (FM) interactions [2]. Recent experimental results of neutron powder diffraction suggest the presence of bond frustration due to competition among several FM and AF interactions in the AF state [3]. It is expected that the orbital degrees of freedom play significant roles in the magnetism of GeCo$_2$O$_4$. 

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We performed ultrasound velocity measurements in GeCo$_2$O$_4$ single crystal in shear and compression moduli. Ultrasound velocity is a powerful tool for the study of orbital physics because the Jahn-Teller (JT) ions strongly couple to the lattice deformations [4]. In addition, since ultrasound wave modulates the distance between magnetic ions, ultrasound velocity is also a directional probe of the anisotropy of exchange interactions acting on the magnetic phase transition [4]. The present study discusses orbital state, spin state, and possible magnetic frustration in GeCo$_2$O$_4$ from the elastic properties.

2. Experimental
Large single crystals of GeCo$_2$O$_4$ were grown by the floating zone method [5]. Néel temperature $T_N$ and Weiss temperature $\Theta_W$ of the single crystal confirmed by the magnetic susceptibility are $T_N = 20.6$ K and $\Theta_W = 11.9$ K, respectively [6]. The ultrasound velocity measurements were performed by the home-built apparatus with the phase comparison technique which can measure the relative change of the ultrasound velocities with high resolution of about 1 part in $10^6$. For the generation and the detection of ultrasounds, LiNbO$_3$ transducers with the fundamental frequency of 30 MHz were glued on the parallel mirror surfaces of the sample by silicone adhesive. Ultrasound velocities were measured in the temperature from 2 K to 100 K.

The ultrasound velocities were measured in five different ultrasound modes in GeCo$_2$O$_4$ single crystal. Table 1 summarizes the ultrasound modes and the corresponding propagation direction $k$, polarization direction $u$, and elastic modulus investigated in the present study. We measured transverse ultrasound velocities in tetragonal shear modulus $(\frac{C_{11}-C_{12}}{2})$ with $E_g$ symmetry, and trigonal shear modulus $C_{44}$ with $T_{2g}$ symmetry. Longitudinal ultrasound velocities were measured in three compression moduli with the different directions of $k$ ($u$) along $[100]$, $[110]$, and $[111]$ directions.

Table 1. Ultrasound modes investigated in this study and the corresponding sound propagation direction $k$, polarization $u$, and elastic modulus in cubic symmetry.

| Ultrasound mode      | $k$       | $u$       | Elastic modulus |
|----------------------|-----------|-----------|-----------------|
| Transverse wave 1    | [001]     | [110]     | $C_{44}$        |
| Transverse wave 2    | [110]     | [110]     | $\frac{C_{11}-C_{12}}{2}$ |
| Longitudinal wave 1  | [100]     | [100]     | $C_{11}$        |
| Longitudinal wave 2  | [110]     | [110]     | $\frac{C_{11}+C_{12}+2C_{44}}{2}$ |
| Longitudinal wave 3  | [111]     | [111]     | $\frac{C_{11}+2C_{12}+C_{44}}{2}$ |

3. Results and Discussion
Figure 1 depicts the temperature dependence of the transverse ultrasound velocities in $C_{44}$ and $(\frac{C_{11}-C_{12}}{2})$ in zero magnetic field. In the paramagnetic state, $C_{44}$ shows steep softening below ~35K down to $T_N$ whereas $(\frac{C_{11}-C_{12}}{2})$ shows slight hardening without any anomaly. Both elastic modes reveal discontinuous anomalies at $T_N$ due to the 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.

In GeCo$_2$O$_4$, the Co$^{2+}$ ($3d^7$) on the octahedral $B$ site contains the orbital degrees of freedom regardless the spin state: threefold-degenerate $t_{2g}$ orbitals in the high spin state ($S = 3/2$), while twofold-degenerate $e_g$ orbitals in the low spin state ($S = 1/2$). If the cubic-to-tetragonal
structural transition at $T_N$ in GeCo$_2$O$_4$ originates from the cooperative JT effect, it is expected that the tetragonal shear modulus $\frac{(C_{11}-C_{12})}{2}$ exhibits a precursor to the transition in the paramagnetic state: a huge softening with decreasing temperature in wide temperature range above the transition temperature [4]. $\frac{(C_{11}-C_{12})}{2}$ in the paramagnetic state shown in Fig. 1, however, exhibits ordinary hardening with decreasing temperature instead of the softening. Since the JT coupling and the intersite orbital-orbital interaction should be present due to the orbital degeneracy of Co$^{2+}$ in GeCo$_2$O$_4$, this JT inactivity indicates that the JT coupling is negligibly weak compared to the orbital-orbital interaction.

The steep softening of $C_{44}$ near $T_C$ shown in Fig. 1 is attributed to the exchange striction effect due to the modulation of the distance between the magnetic Co$^{2+}$ ions by the ultrasound wave written as [4],

$$H_{exx} = \sum_{ij} [J(\delta + u_i - u_j) - J(\delta)] S_i \cdot S_j.$$  \hspace{1cm} (1)

Here $\delta = R_i - R_j$ is the distance between two magnetic ions, and $u_i$ is the displacement vector for the ion $R_i$. Comparing between the high spin state and the low spin state of Co$^{2+}$ on the octahedral $B$ site, both $t_{2g}$ and $e_g$ orbitals can participate in the exchange interactions in the high spin state, whereas only the $e_g$ orbitals can participate in the low spin state. The elastic anomaly of $C_{44}$ with $T_{2g}$ symmetry, therefore, leads to the conclusion that the Co$^{2+}$ in GeCo$_2$O$_4$ adopts the high spin state with $t_{2g}$-orbital degeneracy.

Figure 2 depicts the temperature dependence of the longitudinal ultrasound velocities with the propagation $k || [100]$, $k || [110]$, and $k || [111]$ in zero magnetic field. All the compression moduli exhibit steep softening from $\sim35$ K down to $T_N$ due to the exchange-striction effect of Eq. (1). Among these elastic moduli, the magnitude of the anomalous variation in $k || [111]$ is the largest indicative the strongest contribution of the exchange interactions acting in the $[111]$ direction to the AF transition. This anisotropy of the exchange-striction effect in the paramagnetic state near $T_N$ is consistent with the AF structure with the wave vector $q || [111]$ determined by the neutron scattering experiments [3]. The Goodenough-Anderson-Kanamori rules, however, tell that the presence of a hole in the $t_{2g}$ orbitals in the high-spin Co$^{2+}$ arises
Tetragonal ($c > a$)

Figure 3. Crystal-field splitting by cubic-to-tetragonal structural transition with $c > a$ in the Co$^{2+}$ $(3d^7)$.

Cubic  

Tetragonal ($c > a$)

Figure 4. Geometrical orbital frustration of $t_{2g}$-$t_{2g}$ interaction between the Co$^{2+}$ ions in the Co$^{2+}$ tetrahedron.

The question is why the strong direct-FM interaction competes with the weak distant-neighbors-AF interactions. The most probable answer from the present study is the presence of geometrical orbital frustration in the paramagnetic state in GeCo$_2$O$_4$. In the $t_{2g}$-orbital degenerate system, Kugel-Khomskii-type (KK) FM interaction [8, 9] can be more emphasized since partially filled $t_{2g}$ orbitals have greater degeneracy and weaker JT coupling compared to the $e_g$ orbitals. The JT inactivity strongly suggests the dominant contribution of the orbital-orbital ($t_{2g}$-$t_{2g}$) interaction. It is possible, therefore, that FM transition with orbital ordering occurs in GeCo$_2$O$_4$ by the KK interaction. However, GeCo$_2$O$_4$ exhibits the AF transition, and, as depicted in Fig. 3, the tetragonal elongation below $T_N$ quenches the $t_{2g}$-orbital degeneracy. Thus the possibility of the orbital ordering is ruled out in GeCo$_2$O$_4$. Instead, the tetragonal elongation shown in Fig. 3 can release the geometrical orbital frustration in this compound.

Figure 4 illustrates the schematic picture of the $t_{2g}$-orbital frustration in the Co$^{2+}$ tetrahedron. When a single hole in $t_{2g}$ orbitals is aligned alternately in three Co$^{2+}$ sites of the tetrahedron by the KK interaction, another fourth Co$^{2+}$ site experience the geometrical frustration for the hole (orbital) arrangement. This situation disturbs the occurrence of the orbital ordering. On the other hand, the quenching of the orbital degeneracy by the tetragonal elongation releases the orbital frustration. It is noted that this AF transition with the tetragonal elongation is a new kind of phase transition driven by the orbital degeneracy which is different from the cooperative JT distortion and the orbital ordering.

References

[1] Moessner R and Ramirez A 2006 Phys. Today 59 24.
[2] Diaz S, de Brion S, Holzapfel M, Chouteau G, and Strobel P 2004 Physica B 346-347 146.
[3] Diaz S, de Brion S, Chouteau G, Cannals B, Simonet V, and Strobel P 2006 Phys. Rev. B 74 092404.
[4] Läthi B 2005 Physical Acoustics in the Solid State (Berlin: Springer).
[5] Hara S, Yoshida Y, Ikeda S I, Shirakawa N, Crawford M K, Takase K, Takano Y, and Sekizawa K 2005 J. Crystal Growth 283 185.
[6] Hara S and Ikeda S-I 2007 Private Communications.
[7] J. B. Goodenough, Phys. Rev. 117, 1442 (1960).
[8] Khomskii D I and Kugel K I 1973 Solid State Commun. 13 763.
[9] Inagaki S 1975 J. Phys. Soc. Jpn. 39 596.