Ultrasound velocity measurements in orbital-degenerate frustrated spinel MgV$_2$O$_4$

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Abstract. Ultrasound velocity measurements of the orbital-degenerate frustrated spinel MgV$_2$O$_4$ are performed in the disorder-free high-purity single crystal which exhibits successive structural and antiferromagnetic phase transitions, and in the disorder-introduced single crystal which exhibits spin-glass-like behavior. The measurements reveal coexisting two types of anomalous temperature dependence of the elastic moduli in the cubic paramagnetic phase: Curie-type softening with decreasing temperature, and softening with a characteristic minimum with decreasing temperature. These elastic anomalies should respectively originate from the coexisting orbital fluctuations and spin-cluster excitations.

1. Introduction
Vanadate spinel $A$V$_2$O$_4$ ($A$ = Zn [1], Mg [2] and Cd [3]) is a geometrically frustrated magnet which undergoes a cubic-to-tetragonal structural transition at a temperature $T_s$ and an antiferromagnetic (AF) transition at a low temperature $T_N$. For $A$V$_2$O$_4$, it is considered that the lowering of the lattice symmetry by the structural transition at $T_s$ leads to the release of the frustration by the AF transition at $T_N$ lower than $T_s$. Thus the interplay of spin, orbital, and lattice degrees of freedom should play a crucial role for the release of frustration in $A$V$_2$O$_4$. We are interested in the frustrated phase (the cubic paramagnetic (PM) phase) of $A$V$_2$O$_4$. And we performed ultrasound velocity measurements in the magnesium vanadate spinel MgV$_2$O$_4$. This compound exhibits successive phase transitions of a cubic-to-tetragonal structural transition at $T_s = 65$ K and an AF transition at $T_N = 42$ K [2]. For MgV$_2$O$_4$, it is known that a small amount of disorder suppresses the structural and magnetic phase transitions, and induces spin-glass-like behaviour at low temperatures [4]. In the present study, we performed the measurements in the disorder-free high-purity single crystal with the successive phase transitions at $T_s = 65$ K and $T_N = 42$ K, and in the disorder-introduced single crystal which exhibits the spin-glass-like behaviour below $T_f = 12.5$ K.

2. Experimental
The ultrasound velocity measurements were performed in two different types of MgV$_2$O$_4$ single crystals grown by the floating-zone method: the disorder-free high-purity single crystal with the successive structural and AF transitions at $T_s = 65$ K and $T_N = 42$ K, named here as “ordered MgV$_2$O$_4”,


and the disorder-introduced single crystal with the spin-glass-like behavior below \( T_s = 12.5 \) K in which ~3% of V atoms in the octahedral sites are substituted by Mg atoms, named here as “disordered MgV\(_2\)O\(_4\)” [4]. Temperature (\( T \)) dependence of the ultrasound velocity was measured at \( T \) from 10 K to 150 K with magnetic field \( H/\| [110] \) up to 7 T in all the symmetrically independent elastic moduli in the cubic crystal: compression modulus \( C_{11}, \) tetragonal shear modulus \( (C_{11}-C_{12})/2, \) and trigonal shear modulus \( C_{44}. \) The configuration of propagation \( k \) and polarization \( u \) of the sound wave for each elastic mode is summarized in Table 1.

### Table 1. Elastic modulus of cubic crystal and the corresponding configuration of sound wave with propagation \( k \) and polarization \( u \)

| Elastic modulus                  | Sound wave     | Propagation \( k \) | Polarization \( u \) |
|----------------------------------|---------------|---------------------|---------------------|
| Compression modulus \( C_{11} \) | Longitudinal wave | [001]               | [001]               |
| Tetragonal shear modulus \( (C_{11}-C_{12})/2 \) | Transverse wave | [110] | [110] |
| Trigonal shear modulus \( C_{44} \)       | Transverse wave | [001]               | [110]               |

### 3. Results and discussion

Figures 1(a), (b) and (c) respectively show \( T \) dependence of the compression modulus \( C_{11}, \) the tetragonal shear modulus \( (C_{11}-C_{12})/2, \) and the trigonal shear modulus \( C_{44} \) in the ordered MgV\(_2\)O\(_4\) with \( H = 0. \) All the elastic modes exhibit a jump at \( T_s \) and a discontinuous change at \( T_N, \) as marked by arrows in Figs. 1(a), (b), and (c). In the cubic PM phase \( (T > T_N), C_{11} \) and \( (C_{11}-C_{12})/2 \) exhibit huge Curie-type (\( ~ -1/T \)) softening with decreasing \( T, \) which should be a precursor to the cubic-to-tetragonal lattice distortion at \( T_s. \) As shown in the insets to Figs. 1(a) and (b), this Curie-type softening is independent of \( H \| [110], \) and thus should be driven by the coupling of lattice to orbital fluctuations which is hardly affected by the spin sector [5, 6, 7, 8]. On the other hand, \( C_{44} \) in the cubic PM phase \( (T > T_s) \) exhibits non-monotonic softening with decreasing \( T: \) softening with convex curvature in \( ~80 K < T < ~150 \) K and Curie-type softening in \( T_s < T < ~80 \) K. As shown in the inset to Fig. 1(c), the softening in \( C_{44} \) is sensitive to \( H \| [110]; \) the non-monotonic softening with concave curvature in the \( H \)
exhibit a small increase in slope. In the cubic PM phase (\(T_f\) in Figs. 1(a), (b), and (c). At disordered MgV$_2$O$_4$ should be driven by the coupling of lattice to the spin-cluster excitations. Taking into account that inelastic neutrons scattering experiments in anomaly is usually observed as a result of the coupling of lattice to magnetic excitations [9, 10, 11].

Figures 2(a), (b) and (c) respectively show \(T_f\) dependence of elastic moduli in the disordered MgV$_2$O$_4$ with \(H||[110]\). (a) compression modulus \(C_{11}\), (b) tetragonal shear modulus \((C_{11}-C_{12})/2\), and (c) trigonal shear modulus \(C_{44}\).

\(= 0\) data becomes closer to the Curie-type softening in the 7 T data. Thus, taking into account the \(H\) insensitivity of the Curie-type softening in \(C_{11}\) and \((C_{11}-C_{12})/2\), the non-monotonic softening in \(C_{44}\) should observe a superposition of \(H\)-sensitive concave \(T\) dependence and \(H\)-insensitive Curie-type softening. Furthermore, subtracting the component of the Curie-type softening from the observed non-monotonic softening in \(C_{44}\), another component observed as the concave \(T\) dependence should be characterized as a softening with minimum with decreasing \(T\). Such a softening-with-minimum anomaly is usually observed as a result of the coupling of lattice to magnetic excitations [9, 10, 11].

We here note that the disordered MgV$_2$O$_4$ exhibits the absence of the Curie-type softening, namely the absence of a precursor to structural transition, which is compatible with the absence of structural transition in the disordered MgV$_2$O$_4$. Taking into account the presence of the Curie-type softening in the ordered MgV$_2$O$_4$ as shown in Fig. 1, the present study reveals that not only the structural transition but also its precursor (the Curie-type softening) in MgV$_2$O$_4$ is sensitively suppressed by disorder. On the other hand, the softening with minimum is observed in both the ordered and the disordered MgV$_2$O$_4$ indicating that the spin-cluster excitations are robust against disorder. Therefore the results in the present study strongly suggest the coexistence of the disorder-sensitive orbital fluctuations and the disorder-robust spin-cluster excitations in MgV$_2$O$_4$.

We note here that the component of the softening with minimum in \(C_{44}\) of the ordered MgV$_2$O$_4$ seen in the inset to Fig. 1(c) is sensitive to \(H\), whereas that in \(C_{11}\), \((C_{11}-C_{12})/2\), and \(C_{44}\) of the
disordered MgV$_2$O$_4$ respectively seen in Figs. 2(a), (b), and (c) is insensitive to $H$. This difference in the $H$-sensitivity should also arise due to disorder, where the response of the spin-cluster-lattice coupling to $H$ is quenched by the introduction of disorder. The detailed mechanism for this disorder effect remains to be elucidated. For instance, the excitation in MgV$_2$O$_4$ might correctly be the orbital-spin-cluster excitation, and its change to the orbital-cluster excitation might occur by the introduction of disorder.

4. Summary
We performed ultrasound velocity measurements of MgV$_2$O$_4$ in the disorder-free high-purity single crystal which exhibits successive structural and AF phase transitions, and in the disorder-introduced single crystal which exhibits spin-glass-like behaviour. The measurements reveal coexisting two types of anomalous $T$ dependence of the elastic moduli in the cubic PM phase: Curie-type softening with decreasing $T$, and softening with a characteristic minimum with decreasing $T$. These elastic anomalies should respectively originate from the coexisting disorder-sensitive orbital fluctuations and disorder-robust spin-cluster excitations.

5. Acknowledgement
This work was partly supported by Grant-in-Aid for Scientific Research (C) (25400348) from MEXT of Japan, and by Nihon University College of Science and Technology Grants-in-Aid for Fundamental Science Research.

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