Convergent Beam Electron Diffraction Study on Ge-based Oxide Spinels

S I Ikeda, H Matsuhata, A Tominaga, N Umeyama, S Hara, H Sato, T Watanabe, K Tomiyasu and M K Crawford

1 Nanoelectronics Research Institute, AIST, Tsukuba, Japan
2 Energy Semiconductor Electronics Research Laboratory, AIST, Tsukuba, Japan
3 Department of Physics, Chuo University, Tokyo, Japan
4 Art, Science and Technology Center for Cooperative Research, Kyushu University, Fukuoka, Japan
5 Department of Physics, Nihon University, Tokyo, Japan
6 IMR, Tohoku University, Sendai, Japan
7 DuPont Co., Wilmington, Delaware, USA

E-mail: ikeda-shin@aist.go.jp

Abstract. Transition metal oxides with spinel crystal structure exhibit intriguing and non trivial magnetic phenomena owing to magnetic frustration between spins having antiferromagnetic coupling interaction on triangle or kagome lattice. GeCo$_2$O$_4$ (GCO) and GeNi$_2$O$_4$ (GNO), which belong to above category, are very rare normal spinels containing Ge ion. Both reveal antiferromagnetic-like phase transitions at 20 K and 12 K, respectively. According to previous neutron and x-ray diffraction measurements, GNO keeps its cubic structural symmetry down to 2 K which is not natural because such a magnetic transition tends to associate with symmetry breaking structural transitions. In order to know whether the structural transition or symmetry change occur or not at the magnetic transition in detail, convergent beam electron diffraction measurements is employed for the compounds.

1. Introduction

Magnetic compounds with spinel structure AB$_2$O$_4$ have a wide variety of complex and unprecedented magnetism such as the spin ice or spin liquid states [1,2], since this structure with antiferromagnetic interaction among spins may cause magnetic frustration. Its crystal structure consists of diamond lattice (A site) and pyrochlore lattice (B site). The pyrochlore lattice consists of B site ion tetrahedra as shown in Fig.1. Ge-based normal spinels are known to be very unique since magnetism of GNO and GCO could not be understood by naive interpretations yet. Formally, Co(Ni) ions in GCO(GNO) is divalent with 7(8) electrons in 3d orbitals with spin quantum number $S = \frac{3}{2}$ (1) when orbital quantum number $L$ is quenched as ordinary. Space group of both cubic compounds is $Fd\bar{3}m$.

The first report by Bertaut and Qui on polycrystalline GCO was on neutron diffraction study with a conclusion of the magnetic propagation vector ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) for the antiferromagnetic state [3]. Hubsch et al. argued that the GCO polycrystal demonstrates the first order magnetic transition in magnetic susceptibility and two-dimensional spin fluctuation above the transition temperature [4,5]. Recently, Hoshi et al. reported a structural phase transition from cubic to
Figure 1. Tetrahedral network of Co or Ni sites in the spinel compounds. Ge and oxygen ions are not shown.

Figure 2. Convergent beam electron diffraction patterns at room temperature for (a)GeCo$_2$O$_4$ and (b)GeNi$_2$O$_4$. Electron beam is irradiated along [001] direction.

tetragonal symmetry at $T_N=20$ K by X-ray powder diffraction in addition to induced magnetic anisotropy based on the field dependent magnetization for single crystalline GCO grown by a chemical vapor transport method [6].

As for GNO, Bertaut et al. studied neutron scattering to figure out the spin structure and suggested that antiferromagnetic propagation vector was also $(1/2, 1/2, 1/2)$ [7]. Crawford et al. pointed out that there was no structural phase transition at the first-order magnetic transition around 12 K [8]. Field induced magnetic anisotropy by precise susceptibility measurements was reported by Hara et al. on single crystals grown by a floating-zone (FZ) technique [9]. Matsuda et al. discussed the origin of two consecutive magnetic transitions by means of elastic neutron scattering [10].

For both GCO and GNO, to extract the differences and the common features, large single crystal growth, magnetic and thermodynamic studies were achieved [11-13]. The outstanding point is that GCO yields the structural phase transition and GNO does not. In order to shed light upon this, we have tried to observe electron diffraction patterns on GCO and GNO.
2. Experiment
Single-crystalline samples of GCO and GNO were grown by a floating-zone technique. Due to highly volatile property of GeO$_x$, we tuned conditions of starting composition and pressures for crystal growth. Details of the procedure were already reported [11]. Observation using an electron microscope requires thin specimens prepared by ion milling after mechanical polishing. The observation was carried out using JEM 4000FX operated at 100 kV - 200 kV to reduce radiation damages. Convergent beam electron diffraction (CBED) patterns were obtained at a crystallographic orientation of [001]. In normal transmission electron microscope, at specimen chamber, a leakage of magnetic filed is known to be more or less than 2T by an objective electron lens.

3. Results
Figure 2 displays CBED patterns at the [001] zone axis at room temperature for (a) GCO and (b) GNO. Four-fold rotational symmetry are recognized, however, in detail the symmetry is not perfect. Considering the well-known cubic symmetry of the compounds at the paramagnetic, high temperature region, CBED patterns for [001] axis should have four-fold symmetry. Probably, remained lattice distortion causes the imperfection. To understand this result clearly, observations for other principle axes, [011] and [111], are strongly required.

In this study, we tried to perform low temperature observations using liquid-He sample stage for GeCo$_2$O$_4$. Indication of the temperature were around 13 K, whereas the CBED and parallel beam diffraction patterns did not change. Intensive work will be needed to determine the space group below the magnetic transition temperatures.

4. Conclusion
CBED patterns for GeCo$_2$O$_4$ and GeNi$_2$O$_4$ have been observed. Recognized imperfect four-fold rotational symmetry may be due to residual lattice distortions. Further studies on observations for other axes and for low temperatures where the ground state appears should be performed.

5. References
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