Low-temperature x-ray diffraction studies of $Li_xCu_2O_2$

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1. Introduction

$Li_xCu_2O_2$ has a Cu-O chain structure formed with edge-sharing CuO_4 plaquettes in the *ab* plane while these chains are connected through CuO_2 dumbbells along the *c* direction [1]. This compound is uniquely composed of nearly equal amount of Cu^{1+} and Cu^{2+} simply from the consideration of charge balance, where O-Cu-O dumbbells are formed with Cu^{1+}. The crystal structure was initially misidentified as a tetragonal symmetry due to its severe twinning until it is refined with an orthorhombic symmetry of $a \sim 2b$ [1,2]. Helimagnetic ordering has been identified by neutron scattering along the *b* direction with an incommensurate propagation vector (0.5, ζ = 0.174, 0), where the spin spiral plane is proposed to lie in the *ab* plane with pitching angle of $2\pi\xi \sim 62.6^{\circ}$[3], although the existence of transverse spiral spin component in the *bc* plane is confirmed by Seki *et al*. later[4]. Competing quantum and classical spin periodicity has been explored by neutron scattering, but the proposed important role of intrinsic chemical disorder in this one-dimensional (1D) quantum spin system has not been examined fully yet.

In this work, we investigate the temperature- and field-dependent x-ray powder diffraction (XRD) spectra of single-crystal $Li_xCu_2O_2$. We demonstrate that there is a strong interplay between lattice and spin degrees of freedom in this material.

2. Experimental

Single crystals of $Li_xCu_2O_2$ were grown by the traveling solvent floating zone method. The feed rod was prepared with Li_2Co_3/CuO mixture of molar ratio 1.2:4 and the cold-pressed feed rod is annealed at 850 ℃ for 12 h under oxygen flow. The 20% excess of Li content is used to compensate for the high-temperature Li vapor loss and the crystal growth is presumably through the congruent melt of the feed rod directly. The optimum growth rate has been found to be 3mm/hr and a 20 rpm rotation is maintained. Various gas environments of different Ar/O_2 ratios have been tested in order to achieve single phase growth with specific Li content.

High magnetic field XRD experiments with Co $K\alpha$ radiation were carried at temperature between 10 K and 300 K using a Gifford-McMahon type cryocooler at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University [5]. To accurately determine the structure of the sample and to avoid complications in the analysis due to the domain distribution and twinning, our measurements were performed on powder samples prepared by powdering single crystal.

3. Results and Discussion

Figure 1 shows the zero-field temperature dependence XRD profiles of $Li_{0.87}Cu_2O_2$ in the diffraction angle range of $43.6^{\circ} < 2\theta < 44.3^{\circ}$ with step size of 0.01°. Here, (006) denotes the Miller indices. The $Li_{0.87}Cu_2O_2$ crystal reveals a helimagnetic ordering phase transition temperature ~ 20 K. There is no drastic temperature dependence of a crystal structure. Only upon cooling below 300 K, $Li_{0.87}Cu_2O_2$ shows a decrease of the *a*- and *c*-axis lattice constants, mainly due to the thermal contraction effects. Surprisingly, field-induced changes of XRD (006) peak were found up to 5 Tesla at

10 K, shown in Figure 2. This field-induced effect indicates that lattice and spin degrees of freedom in $Li_{0.87}Cu_2O_2$ are strongly coupled. High-field XRD experiments pose challenges for the interpretation of the large magnetoelastic coupling observed in this material.

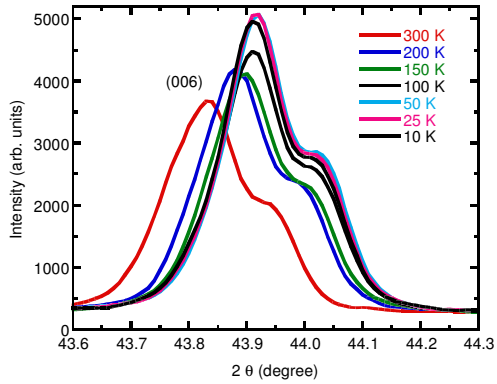

FIG. 1: Temperature dependence of zero-field XRD spectra of $Li_{0.87}Cu_2O_2$.

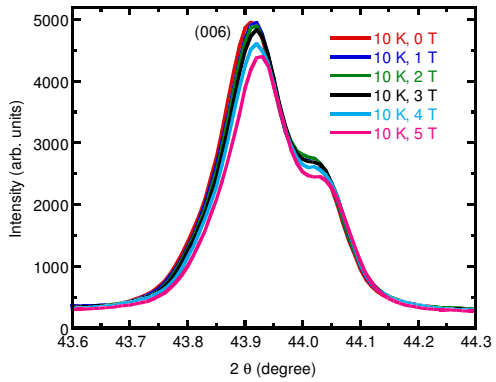

FIG. 2: Field dependence of XRD spectra of $Li_{0.87}Cu_2O_2$ at 10 K.

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