Copper oxide without static Jahn-Teller distortion

The quantum spin liquid (QSL) state has been intensively studied since Anderson proposed the resonating valence bond model. For realizing a novel QSL state, orbital degrees of freedom have been considered a nuisance because orbital ordering usually appears at high temperatures accompanied by cooperative Jahn-Teller (JT) distortion and spin ordering. Therefore, the QSL candidates found so far have been mostly in spin-only systems without orbital degree of freedom: e.g., the two-dimensional kagome systems $SrCr_{9p}Ga_{12-9p}O_{19}$ ($S = 3/2$) and $ZnCu_3(OH)_6Cl_2$ ($S = 1/2$), the two-dimensional triangular lattice system $NiGa_2S_4$ ($S = 1$), the two-dimensional honeycomb lattice system $Bi_3Mn_4O_{12}(NO_3)$ ($S = 3/2$), and the three-dimensional hyperkagome lattice system $Na_4Ir_3O_8$ ($S = 1/2$).

Perovskite-type 6*H*-$Ba_3CuSb_2O_9$ is a novel candidate material for the spin-orbital liquid state, which we have reported recently [1,2]. In the material, spin-orbital short-range ordering occurs in the short-range honeycomb lattice of Cu^{2+} with e_g orbital degrees of freedom, as shown in Fig. 1(a). Powder X-ray diffraction performed at **BL02B2** indicates that even at low temperatures, hexagonal components remain along with some orthorhombically distorted components. In the hexagonal phase, a threefold symmetry exists for Cu^{2+} sites, which are surrounded by octahedrally coordinated oxygen atoms, indicating the absence of a cooperative JT distortion. To explain this unusual feature, we proposed two possible scenarios. (i) A non-cooperative static JT distortion (orbital glass state) appears. In this scenario, the local symmetry is lowered by a static JT distortion, as schematically shown in Fig. 1(b), but the overall hexagonal symmetry remains. (ii) The static JT distortion is absent and instead, a dynamic JT distortion appears, leading to a novel spin-orbital liquid state, as shown in Fig. 1(c). These two possible scenarios cannot be distinguished from experimental results obtained using powder specimens alone. A thorough structural study using a single crystal without orthorhombic components is required.

The progress in preparing single crystalline samples enabled us to obtain single crystalline samples without any orthorhombic components down to the lowest temperature. Figures 2(a) and 2(b) show single-crystal X-ray diffraction experimental data collected at **BL02B1** at 300 K and 20 K, respectively [3]. The peaks show no signs of splitting or broadening down to 20 K ("hexagonal sample"). The hexagonal sample

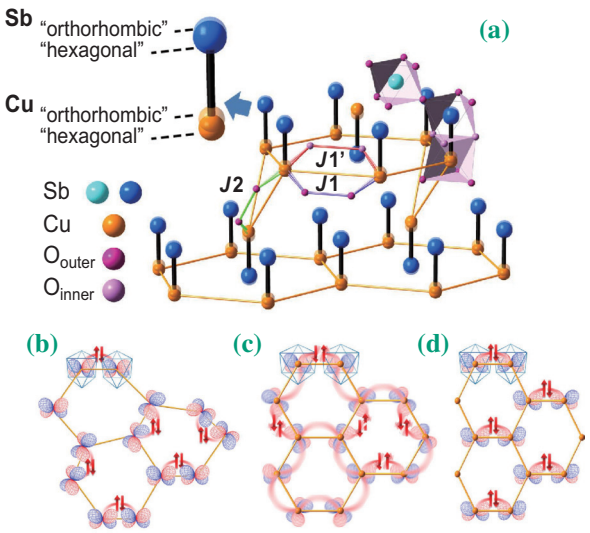

Fig. 1. **(a)** Schematic view of the local structure of hexagonal and orthorhombic samples. **(b)** Schematic image of a non-cooperative static JT distortion. **(c)** and **(d)** Schematic pictures of spin-singlet formation in short-range honeycomb lattices of Cu^{2+} for (c) hexagonal and (d) orthorhombic samples. For (c), a spin-orbital entangled short-range-order state is expected. A pair of upward and downward arrows indicates a singlet state of the dimer based on the neighboring Cu^{2+} spins. At each site, an unpaired electron of Cu^{2+} occupies the $d_{x^2-y^2}$, $d_{y^2-z^2}$ or $d_{z^2-x^2}$ orbital.

can be well refined by using the centrosymmetric space group $P6_3/mmc$ at all temperatures. For $P6_3/mmc$, the threefold symmetry is retained for Cu^{2+} sites, indicating the absence of the cooperative JT distortion. These observations are in sharp contrast with our previous single-crystal X-ray diffraction study of 6*H*-$Ba_3CuSb_2O_9$. In that study, we found that the Bragg peak splits into several separate reflections with decreasing in temperature, as shown in Figs. 2(c) and 2(d). This result indicates that the hexagonal $P6_3/mmc$ symmetry is lowered to the orthorhombic *Cmcm* symmetry ("orthorhombic sample"). We attribute this effect to the cooperative JT distortion induced by the uniform orbital ordering of Cu^{2+} ions (Fig. 1(d)).

To clarify the factor that differentiates the hexagonal samples from the orthorhombic samples, we performed comprehensive studies using ICP-AES and powder X-ray diffraction experiments at beamline **BL02B2** [3]. Although their crystal structures are similar to that of the same space group of $P6_3/mmc$ at high temperatures,

they can be differentiated on the basis of Sb/Cu ratio. As shown in Fig. 3(b), the hexagonal samples are located in the vicinity of the border of the orthorhombic phase, and the JT instability increases with increasing *a*-axis parameter at 400 K and when the Sb/Cu composition ratio slightly deviates from 2/1. When the Sb/Cu ratio is higher than 2/1, some Sb ions replace the Cu ions, which break locally the threefold symmetry of the short-ranged honeycomb lattice. This symmetry breaking inherent to off-stoichiometry induces the orthorhombic distortion at low temperatures. In comparison with the orthorhombic samples, strong geometrical frustration may exist in the hexagonal samples owing to the higher local symmetry. Although the Sb/Cu ratio was found to be always higher than 2/1 in the orthorhombic samples, as shown in Fig. 3(a), the orthorhombic distortion appears even when the Sb/Cu ratio became lower than 2/1.

Although the experimental details are not described here, electron spin resonance (ESR), which sensitively detects the local orbital configuration, has confirmed the isotropic *g* factors within the in-plane directions in the hexagonal samples down to 3.5 K, clearly indicating that the non-cooperative JT scenario is not realized and instead, a dynamic JT distortion appears [3]. Further studies using crystals will address the issues on the quantum spin-orbital liquid state, such as the orbital dynamics and the mechanism that stabilizes such an exotic liquid state.

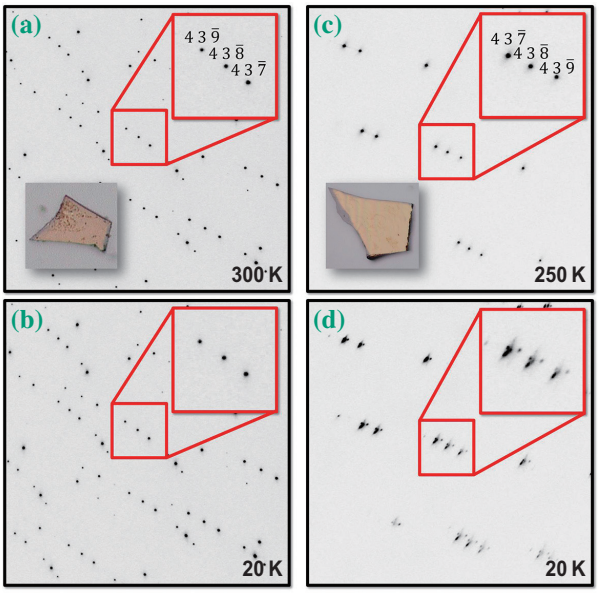

Fig. 2. Single-crystal X-ray diffraction profiles of **(a–b)** hexagonal and **(c–d)** orthorhombic samples. The insets in (a) and (c) are photographs of the transparent brown single crystals for the hexagonal and orthorhombic samples, respectively. The hexagonal samples are darker than the orthorhombic samples.

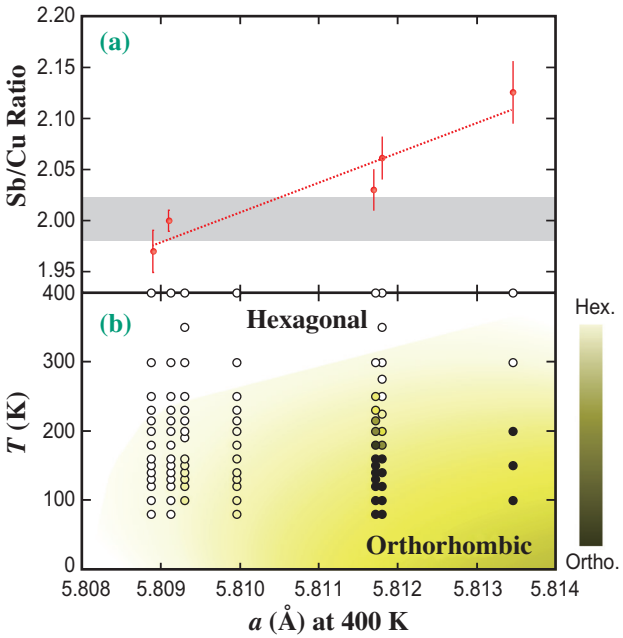

Fig. 3. **(a)** Sb/Cu ratio *vs* lattice parameters of several samples at 400 K. **(b)** Sample dependence on composition ratio between hexagonal and orthorhombic phases examined by decreasing temperature studied using several samples. The vertical axis is the *a*-axis lattice constant obtained at 400 K in the high-temperature hexagonal phase, with which samples are distinguished. Each circle represents a temperature point in powder X-ray diffraction measurements and its color indicates the volume fraction of the hexagonal (white) and orthorhombic (black) phases.

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