

Crystal growth and β -NMR studies of the simplest copper oxide (CuO)

H. Yamazaki,^{*1} A. Gladkov,^{*1} X. G. Zheng,^{*2} A. Yamamoto,^{*3} Y. Ichikawa,^{*1} A. Takamine,^{*1} H. Nishibata,^{*4} K. Asahi,^{*1} K. Kawata,^{*1,*5} K. Imamura,^{*1} M. Tajima,^{*1} K. Tsubura,^{*1} and H. Ueno^{*1}

The significance of oxide-based systems both in technology and basic science has been strongly emphasized. Particularly, the strong electronic correlation caused by Coulomb repulsion in the Cu-O framework is recognized to play a key role in describing many unconventional experimental observations. Even now, however, the origin of the high- T_c superconductivity in copper oxides remains unclear. Meanwhile, another novel function of copper oxide was found about twenty years ago. The simplest copper oxide, CuO (cupric oxide, tenorite), which crystallizes in a monoclinic structure with the space group C2/c, was found to show a cross-correlation effect in one of its magnetically ordered states in the temperature range between 213 K and 230 K.¹⁾ In this so-called “multiferroic” phase, unconventional ferroelectricity emerges with the emergence of specific magnetic ordering.²⁾ The theoretical proposal by Katsura-Nagaosa-Baratzky argues the microscopic polarization of electrons at oxygen sites in association with a noncollinear magnetic structure;³⁾ however, no microscopic evidence of the polarization has been demonstrated so far.

CuO single crystals were grown in quartz tubes using the chemical vapor transport method (Fig. 1).⁴⁾ Using ^{17}O -rich oxygen gas, single crystals of CuO with the oxygen sites substituted with ^{17}O nuclei ($S = 5/2$) were also prepared for comparative ^{17}O -NMR experiments. A large plate-like crystal was typically ~ 10 mm in diameter. SEM images indicate that each crystal is composed of twinned single crystals, in which we can in many cases identify two different rotated images of structural domains with their c -axes nearly perpendicular to the sample plane. X-ray diffraction measurements were carried out to check the quality of the samples in detail. Magnetic susceptibility measurements showed that the magnetic phase transition temperatures and sharpness

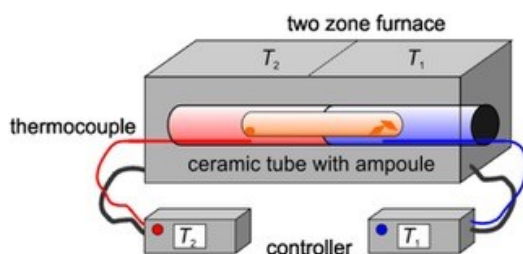


Fig. 1. Conceptual diagram of the chemical vapor transport method for the growth of CuO crystals.

of the transitions were in good agreement with the literature data for high-quality CuO single crystals.

We performed β -NMR/NQR experiments using a ^{21}O ($S = 5/2$) beam, where we used the nuclear reaction $^{22}\text{Ne} + ^9\text{Be} \rightarrow ^{21}\text{O} + \text{X}$ for a ^{22}Ne energy of 70 MeV/nucleon with 250 particle nA. The β -rays emitted from the implanted ^{21}O nuclei were detected with plastic scintillator telescopes located above and below the sample crystal. The resonance frequency can be derived from the peak or dip observed in the spectrum of the up/down ratio of the β -ray count. We were allocated the following accelerator beamtime at the E6 (RIPS) beam port in the RIBF facility: (1) 114 h [2–7 September, 2016] and (2) 111 h [10–14 March, 2020]. The former was mainly used to evaluate the nuclear magnetic moment μ and the nuclear quadrupole moment Q inherent to ^{21}O . Typical NQR spectra are shown in Fig. 2. The following results were obtained: $\mu = 1.5118 \pm 0.0012$ and $Q = 17.4 \pm 2.4$ emb. Based on this achievement, during the latter beamtime, we attempted to obtain the β -NMR spectra for the ^{21}O nuclei implanted in CuO crystals at room temperature. This time, we could not observe a clear NMR signal of ^{21}O in CuO, although our experiments were performed for CuO in the paramagnetic phase ($T > 230$ K). It is considered that the magnetic low-dimensional correlations, which remain up to ~ 550 K,⁵⁾ possibly affected the polarization of the implanted ^{21}O , leading to a reduction of the polarization. At the next beam time allocated in FY2022, we will also have to check some technical issues such as the degree of beam collimation and the thickness of the CuO crystal.

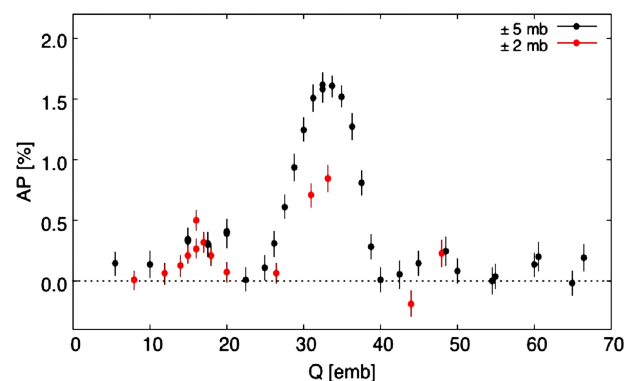


Fig. 2. NQR spectra of ^{21}O in TiO_2 reference crystals.

References

- 1) X. G. Zheng *et al.*, *J. Phys. Soc. Jpn.* **70**, 1054 (2001).
- 2) T. Kimura *et al.*, *Nat. Mater.* **7**, 291 (2008).
- 3) H. Katsura *et al.*, *Phys. Rev. Lett.* **98**, 027203 (2007).
- 4) X. G. Zheng *et al.*, *J. Appl. Phys.* **92**, 2703 (2002).
- 5) T. Shimizu *et al.*, *J. Phys. Soc. Jpn.* **72**, 2165 (2003).

*1 RIKEN Nishina Center

*2 Department of Physics, Saga University

*3 Graduate School of Engineering and Science, Shibaura Institute of Technology

*4 Department of Physics, Kyushu University

*5 Center for Nuclear Study, University of Tokyo