Application of Nuclear Quadrupole Resonance under 10 GPa Class Pressure at Low Temperature

K Hirayama 1, T Yamazaki 1, H Fukazawa 1, Y Kohori 1, N Takeshita 2 and T Matsumoto 3

1Department of Physics, Graduate School of Science, Chiba University, Chiba 263-8522, Japan

2Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, 305-8562, Japan

3ISSP, University of Tokyo, Kashiwa, Chiba, 277-8581, Japan

hirayama_kenji@graduate.chiba-u.jp

Abstract. The high pressure nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are conventionally performed up to 3 GPa using piston cylinder cell. However, the NMR/NQR measurements beyond this pressure range are scarcely performed owing to the technical difficulty. Recently, we developed new high pressure NMR/NQR technique using cubic anvil apparatus with which highly hydrostatic pressure was obtained. Using the new method, the $^{63}$Cu-NQR signal of Cu$_2$O was observed up to 7.2 GPa in nearly hydrostatic condition with high sensitivity. It was noted that the appropriate choice of pressure-transmitting medium is important for accurate experiments.

1. Introduction

Many interesting pressure ($P$) induced quantum-phase transitions such as superconductivity or metal-insulator transition have been observed using diamond anvil cell in which the x-ray or the electric resistivity measurements were performed in a very tiny space. Such a tiny space often prevents the use of other powerful methods. Among them, nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are one of the important techniques. The NMR/NQR under high $P$ were usually performed with piston cylinder cell [1,2]. The large sample space inside the piston cylinder cell is suitable for the NMR/NQR measurements. However, the upper limit of $P$ is only 2-3 GPa which is small and often insufficient for the study of many interesting $P$-induced phenomena. Hence, we developed the new NMR/NQR technique using cubic anvil apparatus with which relatively high $P$ is obtained in the large sample volume with highly hydrostatic pressure condition [3]. We first performed $^{63}$Cu-NQR measurement of Cu$_2$O up to 7.2 GPa. We also compared the several pressure-transmitting media, since the choice of the media affects the $P$ homogeneity [4].
2. Experiment

The $^{63}\text{Cu}$-NQR of Cu$_2$O was measured using a phase-coherent pulsed NQR spectrometer in the resonance frequency range between 26 and 29 MHz. The spin echo signals were Fourier transformed into the frequency domain spectra. For high $P$ measurements, we used mini cubic anvil apparatus which is recently developed by Takeshita et al [5]. The volume of the new system including the cryostat is about 1/30 of the conventional one [6]. The inner sample volume of mini cubic is, however, the same as that of the conventional one. Its maximum pressure is about 10 GPa. The NQR signal was detected by a single-layer coil wound about 20 turns with diameter $\phi = 1.5$ mm and height $h = 0.7$ mm. The commercial Cu$_2$O powder of 99.9% purity was used for the measurement. The Cu$_2$O powder and glycerin were mixed with the ratio of 20 : 1 and set in the detection coil. A mixture of Fluorinert 70 and 77 (Fluorinert) was used as a pressure transmitting medium in mini cubic system.

We also examined more suitable pressure transmitting medium for the mini cubic system. This study was performed with conventional Cu-Be / Ni-Cr-Al hybrid piston cylinder cell. We used the following four representative liquid pressure-transmitting media: Fluorinert, Daphne 7373 oil (Daphne), a 1 : 1 mixture of n-pentane and isopentane (Pentane) and glycerin (Glycerin).

3. Results and Discussion

In Fig. 2, we show the $^{63}\text{Cu}$-NQR spectra of Cu$_2$O measured at room temperature under various $P$ with the use of mini cubic anvil apparatus. With increasing $P$, the spectral center increases and the line width of the spectra also increases. The magnitude of $P$ in Fig.2 was determined by the calibration curve made by Reyes et al. [7] with the calibration formulae $f (P , 300 \text{ K}) = 25.99 + 0.355P - 6.738 \times 10^{-4} P^2$. Here, $f$ and $P$ are in MHz and GPa, respectively. The full width at half maximum (FWHM) of $^{63}\text{Cu}$-NQR spectra at 7.2 GPa is about 140 KHz. The temperature ($T$) dependence of the NMR/NQR is easily performed above about 3 K with this apparatus. Since the NMR/NQR signal intensity increases in inverse proportion to $T$, our high $P$ NMR/NQR system has enough sensitivity to detect most of the signals at the low $T$ region.

The present high $P$ $^{63}\text{Cu}$-
NQR spectra were obtained using Fluorinert as a pressure transmitting medium. The suitable choice of the pressure transmitting medium will increase the $P$ homogeneity. In Fig. 3, we show the $P$ dependence of the FWHM of $^{63}$Cu-NQR spectra of Cu$_2$O with the various pressure transmitting media at room temperature (about 300 K). The most obvious feature of the results is the $P$ dependence of the FWHM obtained in the Fluorinert. The FWHM linearly increases with $P$. The line width is much broader than those obtained in the other three pressure transmitting media. This is ascribable to the fact that the Fluorinert becomes solid above about 1 GPa even at room temperature. Another feature of the results is that the FWHM with Daphne exhibits a slight kink above about 2.2 GPa. This is also due to the fact that the Daphne becomes solid above about 2.2 GPa. Considering the above results and the fact that the Pentane does not become solid up to about 7 GPa, the better hydrostatic pressure can be obtained with the Pentane in these four liquid media. In Fig. 4, we show the $P$ dependence of the FWHM of $^{63}$Cu-NQR spectra of Cu$_2$O with the two different pressure apparatus (cubic anvil apparatus and piston cylinder cell) at room temperature. We can see that cubic anvil apparatus makes not only higher pressure, but also better hydrostatic pressure condition than that of piston cylinder cell.

4. Summary
We demonstrated the $^{63}$Cu-NQR measurements of Cu$_2$O with the use of the mini cubic anvil apparatus. These successful results also suggest that a general NMR/NQR measurement up to about 20 GPa becomes possible by means of a conventional cubic anvil apparatus at low temperatures. We additionally evaluated and compared the pressure quality of the currently representative liquid pressure-transmitting media by performing $^{63}$Cu-NQR measurements of Cu$_2$O. From these results, the better pressure homogeneity is obtained with the pentane as a pressure transmitting medium.
Acknowledgments
This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

References
[1] Fjiwara N, Mori N, Matsumoto Y, Motoyama N and Uchida S 2003 Phys. Rev. Lett. 90 137001.
[2] Fukazawa H, Okazaki T, Hirayama K, Kohori Y, Chen G, Ohara S and Sakamoto I 2007 J. Phys. Soc. Jpn. 76 124703.
[3] Hirayama K, Yamazaki T, Fukazawa H, Kohori Y and Takeshita N 2008 to be published in J. Phys. Soc. Jpn. 77 No.7.
[4] Fukazawa H, Hirayama K, Yamazaki T, Kohori Y and Matsumoto T 2007 J. Phys. Soc. Jpn. 76 125001.
[5] Takeshita N manuscript in preparation.
[6] Mori N, Takahashi H, and Takeshita N 2004 High Pressure Research 24 225
[7] Reyes A P, Ahrens E T, Heffner R H, Hammel P C and Thompson J D 1992 Rev. Sci. Instrum. 78 3120.