Development of Nuclear Magnetic and Quadrupole Resonance Spectroscopy under 10 GPa Class Pressure

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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 in 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 with high sensitivity. The use of MgO gasket in mini-cubic anvil apparatus was examined for enlarging pressure range.

1. Introduction

Many interesting pressure $P$ induced quantum-phase transitions such as superconductivity or metal-insulator transition have been observed using diamond anvil cell with x-ray or electric resistivity measurements in the tiny sample space. However, this sample space is too small for other measurements. 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 is suitable for NMR/NQR measurement. Its available $P$ is 2-3 GPa which is often insufficient for many $P$-induced phenomena. Hence, we developed the new NMR/NQR technique using cubic anvil apparatus [3]. We could perform $^{63}$Cu-NQR of Cu$_2$O up to 7.2 GPa which was nearly upper limit of cubic anvil system with pyrophyllite gasket and tungsten carbide WC anvils. It was reported that the $P$ was enhanced up to 18 GPa when ceramics MgO gasket, which can be commercially obtained from Mino Yougyou company, and sintered diamond anvils were used in cubic anvil system [4]. Here, we examined the use of ceramics MgO gasket instead of pyrophyllite gasket for higher $P$ NMR/NQR.

2. Experimental

The $^{63}$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. The electric resistivity of Bi metal was also measured to determine...
accurate $P$ value from the anomalies of the phase transitions at 2.55, 2.7 and 7.7 GPa. For high $P$
measurements, we used mini cubic anvil apparatus which was recently developed by Takeshita et al
[5]. The new system is much smaller than the conventional one and is easy to handle. Figure 1 shows
the arrangement of cubic anvils. The 6 WC anvils cover all faces of cubic shaped gasket. This
configuration makes a homogeneous $P$ in large volume. The gasket was made of pyrophyllite or MgO,
which has a hole for sample space. The sample is inserted in the Teflon cell together with a liquid
pressure-transmitting media, a 1:1 mixture of Fluorinerts 70 and 77 and then sets in the gasket. We
used same configuration for $^{63}$Cu NQR and resistivity measurements.

![Figure 1. Arrangement of cubic anvil apparatus. All faces of cubic shaped gasket are surrounded by 6 WC anvils. Cubic gasket is made of pyrophyllite or ceramics MgO having cylindrical hole for sample space. The sample sets in Teflon capsule with liquid P transmitting media.](image)

3. Results and discussion

It is difficult to take out the electric leads from the sample space in the high $P$ measurements. The
gasket deformation under $P$ often breaks leads. The hardness of gasket is one of the key factors for available $P$ and the success rate of measurements in the cubic anvil system. The soft pyrophyllite
gasket has a gradual deformation under $P$. The leads made of gold wire or foil is extended gradually
with deformation of gasket, which enable us to perform the measurements at high $P$ with high success rate. On the contrary the hard MgO gasket crushes under $P$ suddenly around 0.1 ~ 1 GPa, which makes heavy damage to electric leads. The measurements using MgO gasket is difficult.

Then we first measured $^{63}$Cu NQR using soft pyrophyllite gasket. The $^{63}$Cu-NQR spectra of Cu$_2$O obtained at room temperature are shown in Fig.2. With increasing $P$, the frequency of resonance line increases and the line width of the spectrum increases. The magnitude of $P$ was determined by the calibration curve made by Reyes et al. [6] with the formula, $f (P, 300 K) = 25.99 + 0.355P - 6.738 \times 10^5P^2$. Here, $f$ and $P$ are in MHz and GPa, respectively. The full width at half maximum (FWHM) of $^{63}$Cu-NQR spectra at 7.2 GPa is about 140 KHz. The

![Figure 2. $^{63}$Cu NQR spectra of Cu$_2$O obtained with cubic anvil apparatus at room temperature.](image)
NMR/NQR measurement at lower temperature, $T$, could be performed with our system since the NMR/NQR signal intensity increases inversely proportional to $T$. The $^{63}$Cu-NQR spectra under high $P$ were obtained using Fluorinert as a pressure transmitting medium. Hence, the inhomogeneous broadening of NQR lines is expected with solidification of liquid Fluorinert above 1 GPa. The observed NQR line width obtained in cubic anvil system is much smaller than that in Bridgeman anvil cell [1]. Even if the solidification of Fluorinert occurs above 1 GPa, the cubic anvil configuration reduces $P$ inhomogeneity appeared in sample space.

We try to measure $^{63}$Cu NQR using MgO gasket since higher $P$ is obtainable. Unfortunately, we could not succeed in spite of many trials. Then we performed resistivity measurement of Bi metal with MgO gasket, which is helpful in finding the suitable condition for performing NMR/NQR. The $P$ dependence of the electrical resistivity, which is plotted against the external load, is shown in Fig.3. The anomalies of the electric resistivity appear at 2.55, 2.7 and 7.7 GPa associated with crystalline structure transitions.

In Fig.4, we also plotted $P$ evaluated from $^{63}$Cu NQR against the external load of mini cubic anvil apparatus with pyrophyllite gasket. The $P$ induced in soft gasket is proportional to the load below 3 GPa and has a tendency to saturate at higher $P$. The maximum $P$ in our system is 7 GPa. The $P$, which is evaluated from electrical resistivity of Bi metal, obtained with MgO gasket is also shown in Fig.4. It is remarkable that no saturation behaviour appears in MgO gasket case up to 8 GPa. Up to now, we could not succeed to observe NMR/NQR in MgO gasket. The use of new gasket will certainly enhance the maximum $P$ value up to 10 GPa in our cubic anvil system without changing WC anvil into the sintered diamond one.

4. Summary

We demonstrated that the $^{63}$Cu-NQR in Cu$_2$O is possible up to 7 GPa with the use of the mini cubic anvil apparatus. The cubic anvil configuration suppresses the $P$ inhomogeneity in the sample space.
The Bi metal resistivity measurement indicates $P$ would increase up to 10 GPa by only changing the gasket to ceramic MgO.

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