Appropriate pressure-transmitting media for cryogenic experiment in the diamond anvil cell up to 10 GPa

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Abstract. We evaluated the qualities of pressure-transmitting media by the ruby fluorescence method at room temperature, 77 and 4.2 K in the diamond anvil cell (DAC) up to 10 GPa in order to find appropriate media for the low temperature experiment. Investigations were done on fourteen kinds of media: a 1:1 mixture by volume of Fluorinert FC-70 and FC-77, Daphne 7373 and 7474, NaCl, silicon oil (polydimethylsiloxane), vaselin, 2-propanol, glycerin, a 1:1 mixture by volume of n-pentane and isopentane, a 4:1 mixture by volume of methanol and ethanol, petroleum ether, nitrogen, argon and helium. We discuss the non-hydrostatic effects of the pressure in the media from the broadening effect of the ruby $R_1$ fluorescence line. At the low temperature region, the non-hydrostatic effects develop continuously with increasing pressure from the low-pressure region in the all media. We reveal the relative strengths of the non-hydrostatic effects appeared in the media at 77K.

1. Introduction
High pressure studies with a diamond anvil cell (DAC) have developed extensively in various fields of science, including physics, chemistry, geophysics, materials science and biology [1]. The DAC technology have been successfully applied to the low temperature physics where many interesting pressure-induced phenomena such as the superconductivity have been discovered [2].

In the high-pressure study, non-hydrostatic effects such as pressure inhomogeneous distribution and uniaxial stress should be reduced because the physical properties of a sample are strongly influenced by the effects. It is important to use a media in a pressure region where it is in the liquid state in order to ensure a hydrostatic pressure. However, a fluid medium becomes solid in a cooling process from room temperature to a low temperature region. One cannot avoid the non-hydrostatic effects in a cryogenic experiment. There have sometimes reported discrepancies in experimental results such as a pressure phase diagram in the field of a low temperature science. One of reasons for the discrepancies may be the non-hydrostatic effects of the pressure.

We have evaluated the pressure-qualities of media for the low temperature physics, especially for the study of a strongly correlated electron system where novel types of physical phenomena such as an unconventional superconductivity has been studied extensively [3]. The electronic state of the system is generally sensitive to small amounts of impurities or non-hydrostatic effects. We introduce a recent example of “FeAs-based superconductor” CaFe$_2$As$_2$ where the...
supercritical state was discovered above 0.5 GPa in a high-pressure study using organic media [4], while it was not observed in a helium medium [5]. The confused results may come from the sensitive structural instability to the uniaxial stress of the compound. Unfortunately, most of previous studies on the pressure-media have been done for the determination of a hydrostatic limit pressure at room temperature [6, 7]. Since one cannot escape from the non-hydrostatic effects in the low temperature region, it is important to know the relative strengths of the non-hydrostatic effects appeared in pressure-media. So far, only a few studies have been carried out for the pressure-qualities of media at the low temperature region up to 3 GPa [8, 9]. In this study, we evaluated the (non-) hydrostaticity of fourteen kinds of pressure-transmitting media by the ruby (Al$_2$O$_3$: Cr$^{3+}$) fluorescence technique up to 10 GPa at room temperature, 77 and 4.2 K.

2. Experiment

We have investigated fourteen kinds of media: a 1:1 mixture by volume of Flourinert FC-70 and FC-77 (Flourinert FC70/77, Sumitomo 3M), Daphne 7373 and 7474 (Idemitsu), NaCl, vaselin, silicon oil (polydimethylsiloxane with the kinematic viscosity of 1 mm$^2$s$^{-1}$, Shin-Etsu Chemical), 2-propanol, glycerin, a 1:1 mixture by volume of n-pentane and isopentane (pentane mixture), a 4:1 mixture by volume of methanol and ethanol (4:1 M-E mixture), petroleum ether (Wako Chemical Industries Ltd.), nitrogen, argon and helium. The strengths of the non-hydrostatic effects in the media were evaluated from the broadening of the ruby $R_1$ fluorescence line using a clamp-type diamond anvil cell originally designed by Dunstan and Spain [10, 11]. The culet size of diamonds and the diameter of a sample chamber are 800 and 400 $\mu$m, respectively. The ruby fluorescence was measured using a charged coupled device (CCD) spectrometer. The diode pumped solid-state (DPSS) green laser light (532 nm) enters the sample chamber through a fiber optics and excites small ruby chips uniformly placed in the sample chamber [12]. The diameters of the chips are less than 10 $\mu$m. We confirmed the chip as a single crystal by the X-ray diffraction analysis. The diameter of a beam line is 600 $\mu$m, larger than the diameter of the sample chamber. The broadening of the ruby $R_1$ peak reflects the spatially averaged information for non-hydrostatisity of the pressure inside the chamber. It is to be noted that the pressure shifts of the ruby $R_1$ line are sensitive to the uniaxial stresses [13, 14]. The broadening of the ruby $R_1$ line in the present study reflects both the inhomogeneous pressure distribution and uniaxial stress pressure since the directions of the single crystals are randomly oriented in the chamber.

We describe differences between the present work and previous studies. The pressure distribution inside the sample chamber was carefully studied at room temperature in the well known paper of the ref. 6 [6]. The ref. 7, 8 and 9 reported spatially local information of the non-hydrostatic effects around the center position of the chamber since the size of “sensors” to detect the effects such as ruby chips, Cu$_2$O or NaCl were very small compared the sample space [7, 8, 9]. This work clarifies the spatially averaged information of the non-hydrostatic effects inside the sample chamber at the low temperature region. The observed broadening effect reflects both pressure inhomogeneous distribution and uniaxial stress. Main concern of the previous work is to determine the hydrostatic limit pressures of media at room temperature. We try to clarify the relative strengths of the non-hydrostatic effects in the low temperature region where one cannot escape from the effects.

The positions and widths of $R_1$ and $R_2$ lines were determined by deconvoluting measured $R$-line spectra into a pair of pseudo-Voigt functions that represent the contribution of the ruby $R_1$ and $R_2$ lines with a linear background. The spectra were measured at room temperature, 77 and 4.2 K (nitrogen, argon and helium only). We applied and changed the pressure at room temperature. The clamped DAC was cooled down to 77 and 4.2 K slowly using liquid nitrogen and helium, respectively. We have studied the pressure dependence of the width of the ruby
R\textsubscript{1} line for two or three times with independent settings for each medium. The pressure was determined by the pressure shift of the ruby R\textsubscript{1} line using a hydrostatic ruby pressure scale by Zha, Mao and Hemley [15].

### 3. Results and discussions

We show the results of the representative medium glycerin in Figure 1 (a) and (b). The suitability of glycerin as the pressure-medium was examined up to 7 GPa by a neutron diffraction study at room temperature [7]. However, there is no clear report for the hydrostatic-limit pressure of the medium even at room temperature. Fukazawa et al., evaluated the medium by the NQR spectra at 4.2 K up to 2.5 GPa [8]. We show the fluorescence spectra of the ruby R lines for the representative medium glycerin in Figure 1 (a). The pressure dependences of the full-width at half maximum (FWHM) of the ruby R\textsubscript{1} line at room temperature and 77 K are shown in Fig.1 (b). Lines of the figure are fits to the pressure dependence of the FWHMs with poly-nominal functions. The ruby R\textsubscript{1} line begins to become broadened above the liquid-solid transition pressure of about 5 GPa at room temperature [16]. The hydrostatic limit pressure of the glycerin medium is determined as 5 GPa at room temperature. The FWHM at 77 K shows a complex behavior: it increases non-lineary below 1 GPa, tends to saturate above 2 GPa, and re-increases strongly with increasing pressure above 5 GPa. This suggests the strong non-hydrostatic effects in the medium above 5 GPa at the low temperature region.

To compare the strengths of the non-hydrostatic effects in the media, we discuss the value of ΔFWHM: a relative increase of the R\textsubscript{1} line width to the ambient value. We show the pressure dependences of ΔFWHMs at 77 K in Figure 2. We obtain the lines of ΔFWHMs in the figure by subtracting the ambient value from the fitting functions of the FWHMs. Error bars indicate averaged deviations of experimental data from the fitting lines at each pressure. At 77 K, the ΔFWHMs increase continuously from the low-pressure region below 1 GPa, indicating that the
Figure 2. (Color online) ΔFWHM of the ruby $R_1$ line for fourteen kinds of pressure-media at 77 K. Lines are obtained from the fittings of the FWHMs of the media. Error bars indicate averaged deviations of the experimental data from the lines at each pressure.

non-hydrostatic effects start to develop even from the low-pressure region at the low temperature region. This is contrary to the pressure dependences of the FWHMs at room temperature where it starts to increase generally above the solidification pressure.

We classified the media into three groups (I, II and III) from the values of ΔFWHM at 5 GPa and 77 K. At first, we discuss results on the media in a group I: Fluorinert FC70/77, Daphne 7373, NaCl, silicon oil and vaselin. Previous studies show advantages of the media for the high-pressure experiment in the low-pressure region [6, 17, 18, 19]. The ΔFWHMs of the media show a large value of above 0.3 nm at 5.0 GPa, indicating the strong non-hydrostatic effects. The ΔFWHMs of Daphne 7373, silicon oil and vaselin show smaller values less than 0.1 nm below 2.0 GPa, indicating that the media are acceptable for the low-pressure region. The FWHMs of silicon oil and vaselin increase largely above 2.0 GPa, although the FWHMs of the media do not show a significant increase at room temperature [19, 20]. The ΔFWHMs of NaCl shows a rapid and non-linear increase below 1 GPa. The results suggest that the media in the group I are not suitable for the cryogenic experiment with the DAC in the higher-pressure region.

Next we discuss the results of the media in a group II: 2-propanol, glycerin and Daphne 7474. It was clarified by previous studies on 2-propanol and Daphne 7474 that pressure distributions inside sample chambers filled with the media become inhomogeneous roughly above 4 GPa at room temperature [6, 21]. In our study at 77 K, there is no strong increase in the pressure dependence of the ΔFWHMs in the media below 5 GPa. The values of ΔFWHMs at 5.0 GPa are 0.12, 0.18 and 0.14 nm for 2-propanol, glycerin and Daphne 7474, respectively. These values are less than half of those of the media in the group I. However, the ΔFWHMs increase strongly with increasing pressure above 5 GPa and show values comparable with those of the media in the former group. It is suggested that the media are appropriate for the cryogenic experiment below 5 GPa. We note that the value of ΔFWHM for glycerin is larger than those of some media in the
group I below 2 GPa. For example, the values of glycerin medium at 1.5 GPa is 0.08 ± 0.01 nm, larger than 0.02 ± 0.01 nm and 0.05 ± 0.01 nm for Daphne 7373 and silicon oil, respectively at the same pressure. The strengths of the non-hydrostatic effects in the glycerin medium is larger than those of the two media below 2.0 GPa. This is consistent with the previous evaluation of pressure-media by the $^{63}$Cu-NQR spectra of Cu$_2$O at 4.2 K [8]. It was reported that the FWHM of the spectra for the glycerin medium is about 1.5 times larger than that for Daphne 7373 below 2 GPa at 4.2 K.

We show the results of media in a group III: the pentane mixture, the 4:1 M-E mixture, petroleum ether, nitrogen, argon and helium. The three organic media have been known as good media for the high pressure study at room temperature [6, 22]. The hydrostatic limit pressures are determined as 7.3 and 10 GPa for the pentane and 4:1 M-E mixtures, respectively, at room temperature. There has been no study for the hydrostatic limit pressure of petroleum ether as far as we know. The three elements nitrogen, argon and helium have been also known as good pressure-media at room temperature [23, 24, 25]. Burnett et al. studies the suitability of the elements as the pressure-medium in the cryogenic experiment at 4.2 K up to 3 GPa. It was shown that helium does not give non-hydrostaticity even at the temperature and that argon gives slightly less hydrostaticity [9]. There has been no study on nitrogen for suitability as the pressure-medium in the low temperature experiment as far as we know. We evaluated the media up to 10 GPa at 77 K.

The ∆FWHMs of the media at 77 K do not show a strong increase below 10 GPa, suggesting that the media are more suitable for the cryogenic experiment. In particular, the value of the ∆FWHM for petroleum ether is the smallest among the organic media. The present study also reveals that nitrogen, argon and helium show less non-hydrostatic effects in the low temperature region up to 10 GPa than the other media do. The value of ∆FWHMs is 0.10, 0.14 and 0.05 nm for nitrogen, argon and helium, respectively, at 10 GPa. These values are less than 20 % of those of the Fluorinert FC70/77 and Daphne 7373 at the same pressure. We measured the fluorescence spectra of nitrogen, argon and helium at 4.2 K (data not shown) and confirmed that the values of ∆FWHMs are the same as those at 77 K within experimental errors [20]. This work clarifies the suitability of the three elements as the media even in the low temperature region up to 10 GPa.

Very recently, eleven kinds of pressure-media were systematically evaluated by the ruby fluorescence method at room temperature by Klotz et al [26]. The reported pressure dependences of the widths Γ of the ruby $R_1$ line are consistent with those of our data for the pentane and 4:1 M-E mixtures, silicon oil, Daphne 7474, nitrogen, argon and helium at room temperature (data not shown). A weak deviation from the homogeneous pressure associated with the solidification of the media was carefully estimated from the $R_1$ lines of several ruby spheres placed in the sample chamber. It was reported that the small pressure gradient $\sigma$ starts to develop in the argon medium above 2 GPa at room temperature even though the width of the ruby $R_1$ line does not show a clear broadening effect. They concluded that the hydrostaticity of the pressure in the argon medium is worse than that in the nitrogen medium at room temperature. Unfortunately, we can not detect such small pressure gradient in our study since the broadening effect of the ruby $R_1$ line reflects the spatially averaged information for the non-hydrostatic effects in the sample chamber. We note that the less hydrostaticity of the argon medium compared with that of the nitrogen one becomes evident above 8 GPa at 77 K in our study. The weak derivations from the homogeneous pressure in the media were thoroughly studied at room temperature in Klotz’s work. On the other hand, our purpose of the present study is to reveal the relative strengths of the non-hydrostatic effects appeared in the fourteen kinds of media at the low temperature region where we cannot escape from the effects.

Finally, we mention some notes for better interpretations of the present results.

(1) One can apply the present results to the high-pressure study using opposed anvil type
high-pressure cells (the DAC and Bridgman cell). But it may not be applied simply to the study using a multi-anvil type high-pressure cell where a sample with the medium is pressed by six or eight anvils. Generally, the better pressure quality is expected for the multi-anvil type cell [28].

(2) The ruby crystal is relatively stiff material with the bulk modulus of 253 GPa [27]. If a material to be studied is strain sensitive or it has mechanical strengths smaller than those of the ruby crystal, the non-hydrostatic effects can have a bad influence on the physical properties of the material even though the broadening of the ruby $R_1$ peak is small and absent.

(3) Some organic media in the group II and III may react chemically with organic materials. There is a possibility that small argon and helium atoms penetrate into a sample with a cage structure like fullerenes of C$_{60}$ and C$_{70}$ [29].

Summary
We evaluated fourteen kinds of the pressure-transmitting media by the ruby fluorescence method at room temperature, 77 and 4.2 K in the diamond anvil cell (DAC) up to 10 GPa in order to find appropriate media for the low temperature experiment. Our studies clarifies the relative strengths of the non-hydrostatic effects appeared in the media. It was found that the media in the group III (the pentane mixture, the 4:1 M-E mixture, petroleum ether, nitrogen, argon and helium) show less non-hydrostatic effects compared with the media in the other groups. Some notes for the better understanding of the present results are given.

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