

Solid-state ^{197}Au NMR of gold metal

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ABSTRACT.

Solid-state ^{197}Au static nuclear magnetic resonance (NMR) spectra of gold metal, detected at 18.79666 T and at room temperature, have been presented. Thermal annealing process plays an essential role for observation of the ^{197}Au NMR signals. A single peak at $13.937275 \text{ MHz} \pm 25 \text{ Hz}$ is observed and the Knight shift at room temperature is determined to be 0.11 %. The Knight shift at 4 K is redefined to be 0.07 %, using the modern physical constants.

INTRODUCTION

Solid-state ^{197}Au nuclear magnetic resonance (NMR) spectroscopy is expected to become a powerful tool for investigation of gold metal and associated alloys. However, there have been very few literature studies on solid-state ^{197}Au NMR, due to unfavorable nuclear properties of ^{197}Au (nuclear spin number (I) = 3/2, natural abundance = 100 %, NMR frequency ratio Ξ = 1.729 %¹, nuclear magneton quadrupole moment (Q) = 54.7 fm²). Indirect solid-state NMR measurements have been often used for investigations of gold complexes^{2,3}. Apparently, solid-state ^{197}Au NMR measurement of gold metal was only reported in the 1960s. Narath⁴ presented the first ^{197}Au NMR spectrum of gold metal observed at 4 K, from which the Knight shift, which refers to the relative shift in a metal compared in non-metallic environment, was obtained. To the best of our knowledge, no literature except for the result at 4 K has been published for solid-state ^{197}Au NMR of gold metal. Moreover, the Knight shift was previously calculated with the older values of physical constants, which have subsequently been revised, so that the redefinition is needed. In this paper, solid-state ^{197}Au NMR spectra of gold metal observed at room temperature have been presented for the first time. The Knight shift is obtained and that at 4K is redefined using the latest physical constants.

EXPERIMENTAL

Gold foil (99.95 %) with a thickness of 0.02 mm was purchased from The Nilaco Corporation (Tokyo, Japan), and used without further purification. The gold foil was cut into small pieces about 10 × 1 mm. Samples were placed in an alumina crucible and thermally annealed in air at 523 K, 623 K, and 773 K for 1 hour each. Approximately 150 mg of the sample was packed into a glass tube with a diameter of 4 mm, and the end was sealed by plastic end-cap. A 70-turns of copper wire (0.1mm in diameter) was wound around the sample tube, which was set to a home-made NMR probe. A superconducting magnet from an 800 MHz NMR equipment manufactured by JEOL Ltd. (Tokyo, Japan) was used, and the magnetic field strength was calculated to be 18.79666 T from a resonant frequency of deuterium in D₂O, 122.8531 MHz. THAMWAY NMR Spectroscopy Measurement Systems (Shizuoka, Japan), was used for all the NMR experiments. A solid echo sequence, $\pi/2$ - τ_1 - $\pi/2$ - τ_2 -ACQ was employed to detect ¹⁹⁷Au NMR signals at 13.935 MHz with the following parameters: $\pi/2 = 10 \mu\text{s}$, $\tau_1 = 250 \mu\text{s}$, $\tau_2 = 10 \mu\text{s}$, spectral width = 2.5 MHz, number of scans = 115,200, and recycling delay time = 0.5 s. After left-shifting of an FID signal and zero-filling, Fourier transform processing was performed.

Results and Discussion

Figure 1 shows the solid-state ^{197}Au static NMR spectra of gold metal: a sample with non-thermal annealing and ones with thermal annealing at 523, 623 and 773 K for 1 hour each, from bottom to top, respectively, detected at 18.79666 T and room temperature (300 K). A single sharp peak at $13.937275 \text{ MHz} \pm 25 \text{ Hz}$ can be observed for samples with annealing at 623 K and 773 K, while no peak and very weak one for those with non-thermal annealing and annealing at 523 K, respectively. The presence or absence of a signal in Figure 1 implies that sufficient heat treatment is essential for ^{197}Au signal detection of gold metal. In an as-is sample, *i.e.*, no treatment of thermal annealing, the gold atom sites are not in environments of high Platonic/spherical symmetry due to strain.^{5,6} This makes it very difficult to observe ^{197}Au NMR spectra, since the spectral width is broadened by large quadrupolar interactions. In annealed samples, on the other hand, as the annealing temperature increases, the distortion of the face-centered cubic (fcc) lattice structure gradually decreases, which results in smaller quadrupolar interaction, *i.e.*, a sharp peak. Similar effect of thermal annealing process has been reported for electron microscopy of gold metal⁷.

The nominal nuclear gyromagnetic ratio of ^{197}Au in gold metal at room temperature can be determined to be 0.7414761 MHz/T from the above resonant frequency, which is almost the same as that at 4 K reported by Narath⁴, 0.074119 kHz/Oe . It is important to point out that the difference in the nuclear gyromagnetic ratio between the room temperature and 4 K is only 0.04 %.⁸

NMR shifts in metals were first reported by W. D. Knight.⁹ The relatively large NMR shift in metals is called the Knight shift and given by,

$$\text{Knight shift} / \% = (\mu_{\text{metal}} - \mu_{\text{atom}}) / \mu_{\text{atom}} \times 100 \quad [1]$$

where μ_{metal} and μ_{atom} are nuclear magnetic moment of gold atom in pure metal and free gold atom, respectively. μ_{metal} is given by

$$\mu_{\text{metal}} = \gamma_{\text{metal}} \times J \quad [2]$$

where γ_{metal} and J are effective gyromagnetic ratio of gold metal and a total angular momentum, respectively, given by

$$\gamma_{\text{metal}} / 2\pi = (\text{resonance frequency of gold metal}) / (\text{applied magnetic field}) \quad [3]$$

and

$$J = h / (2 \pi) \times I \quad [4]$$

where h is Planck's constant of $6.62607015 \times 10^{-34} \text{ J}\cdot\text{s}$ ¹⁰ and I is nuclear spin number. μ_{atom} is $0.145746 \mu_{\text{N}}$ ¹¹, where μ_{N} is nuclear magneton. The present value of μ_{N} is $5.05078324 \times 10^{-27}$

J/T.¹¹ From the present results, μ_{metal} can be calculated to be $0.1459102 \mu_{\text{N}}$. If the present μ_{metal} at

room temperature and μ_{atom} reported by Narath⁴ are used for it, the Knight shift at room

temperature is calculated to be 1.68 %, which is consistent in that at 4 K in the literature⁴.

However, the Knight shift at room temperature is determined to be 0.11 %, when the present

μ_{atom} is used. Moreover, if the present μ_{atom} and μ_{metal} reported by Narath⁴ are used, the Knight

shift at ~~room temperature~~ 4K becomes 0.07 %, which leads to the fact that the nuclear

gyromagnetic ratio between room temperature and 4 K is 0.04 %, Therefore, it can be concluded

that the Knight shift at 4K is redefined to be 0.07 %, which is inconsistent in the literature value

of 1.64 % reported in 1967⁴. We believe that the discrepancy stems from the difference in

constants used for calculations. In the literature, μ_{atom} of $0.143491 \mu_{\text{N}}$ and nuclear magneton μ_{N} of $5.05050 \times 10^{-24} \text{ erg/G}$, which are different values at the present time of $\mu_{\text{atom}} = 0.145746 \mu_{\text{N}}$ and $\mu_{\text{N}} = 5.05078324 \times 10^{-27} \text{ J/T}$, were employed.

CONCLUSION

Solid-state ^{197}Au static NMR spectra of gold metal with thermal annealing at 623 K and 773 K for 1 hour each have been observed at room temperature. Thermal annealing process is essential for detection of the ^{197}Au NMR signals, and the nominal nuclear gyromagnetic ratio of ^{197}Au in gold metal at room temperature is found to be 0.7414761 MHz/T. Using modern physical constants, the Knight shift at room temperature is determined to be 0.11 %, and that at 4 K is redefined to be 0.07 %.

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FIGURE CAPTION

Figure 1 Solid-state ^{197}Au static NMR spectra of gold metal: a sample with non-thermal annealing and ones with thermal annealing at 523 K, 623 K and 773 K for 1 hour each, from bottom to top, respectively, detected at 18.79666 T and room temperature (300 K).

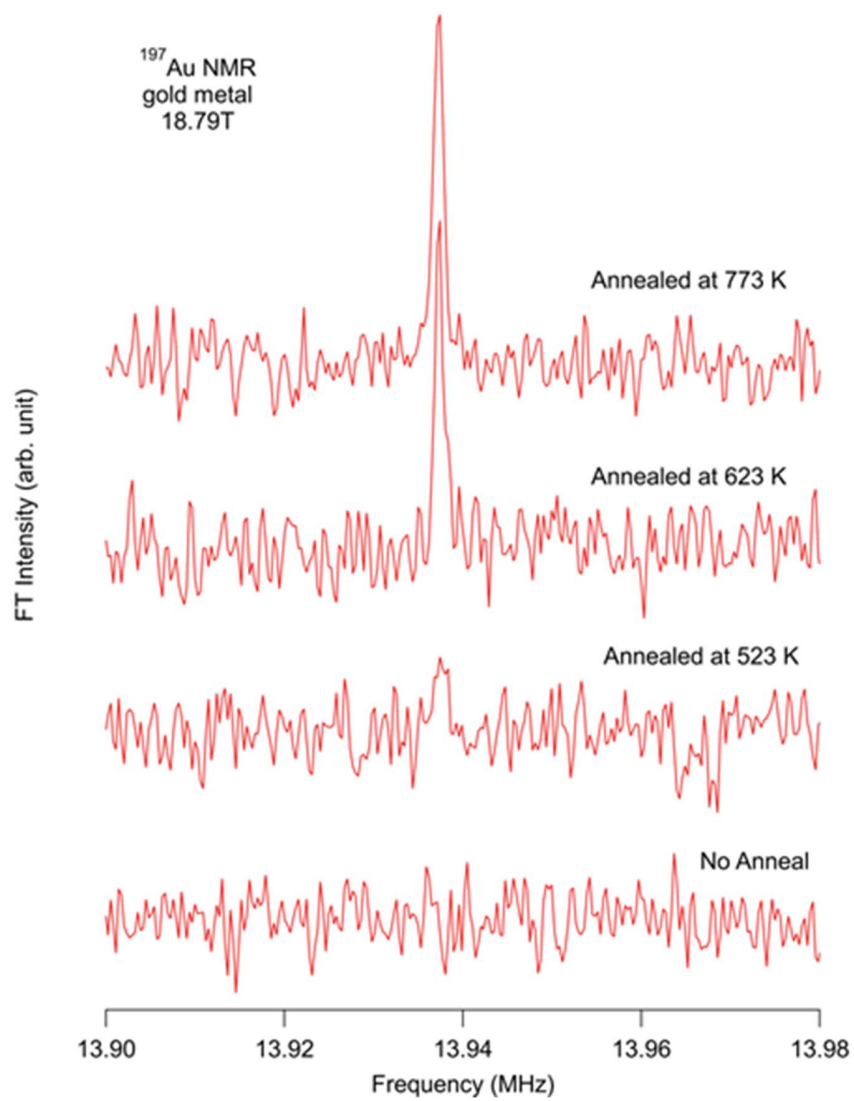


Figure 1