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Dielectric Properties of Twisted Nematic Liquid Crystal Displays Fabricated by Doping Ag-Pd Metal Nanoparticles Having A Long Term Stability

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TN-LCDs particularly doped with the metal nanoparticles of Ag-Pd composite, which are protected by chemical covering with nematic liquid crystal, 5CB (K-15, Merck) as a ligand, are shown to exhibit a long term stability in the electro-optical (EO) effect featured by a frequency modulation with short response times of ms or sub-ms order. This device is called FM-LCD. The unique electro–optical characteristics of the FM-LCD were clarified in terms of the Maxwell-Wagner effect of a heterogeneous dielectrics, where the analysis is done using an equivalent circuit model rather than the conventional potential theory; and we derived the formulae of the dielectric strength and the dielectric relaxation time. The former is used to explain the FM-LCD effect and also to evaluate the effective electrical conductivity of the metal nanoparticle that will be $4.4 \times 10^4 S/m$*, which is about* 1×10^{-3} *times smaller than that of metal Ag; and the latter is expressed to demonstrate that the relaxation time decreases with increasing the concentration of metal nanoparticle for the first time.*

Keywords: equivalent circuit model; FM-LCD; liquid crystal; metal nanoparticles; Maxwell–Wagner effect; TN-LCD

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1. INTRODUCTION

In a previous paper, the author's research group reported that liquid crystal displays (LCDs) such as TN-mode LCD and TB-mode LCDs exhibit a frequency modulation electro–optic (EO) response (called FM-LCDs); [1–5] and these devices exhibit fast EO response with the response times of ms or sub-ms order [3]. The present paper describes and discusses on the synthesis of the NLC(5CB, K-15 Merck) protected metal nanoparticles of Ag-Pd composite that has a long term stability better than Ag alone; the fabrication of the FM-TN-LCD doped with the Ag-Pd nanoparticles; the E-O characteristics of the FM-TN-LCD; and the theoretical study of the dielectric properties of the FM-TN-LCD cells based on an equivalent circuit model and a crystal model [6]. This approach makes it possible to show that the dielectric relaxation time decreases with increasing the concentration of metal nanoparticles. Whilst, the conventional theories, which are formulated using potential theory, are unable to demonstrate this concentration dependence [7–10]. Further, this paper also discusses the effective electrical conductivity of metal nanoparticles based on the equivalent circuit model together with the Drude model and Kawabata and Kubo theory [11]; and it is shown that the metal nanoparticle of Ag–Pd composite has the effective electrical conductivity of 4.4×10^4 S/m that is about 1×10^{-3} times smaller than that of metal Ag.

2. EXPERIMENTALS

2.1. Synthesis of Ag-Pd Nanometal Particles

Nematic liquid crystal, 5CB (K–15, Merck) protected Ag-Pd bimetallic nanoparticles were synthesized by the following way: 4-Cyano-4′–n-pentylbiphenyl (5CB, 1.32 mol, 40 times of the total amount of metal ions), silver(I) perchlorate ($AgClO_4$, 0.0166 mmol), and palladium(II) acetate ($Pd(CH_3COO)_2$, 0.0166 mmol) were mixed in tetrahydrofuran (THF) to form a 50 cm^3 solution; and the mixed solutions in a quartz vessel were degassed by three freeze-thaw cycles and filled with pure nitrogen; and then they were exposed to a UV light source of a super-high-pressure mercury lamp (Ushio, 500 W) for 2 h in a water bath.

2.2. Characterizations

Ultraviolet and Visible (UV-Vis) Spectra were obtained at room temperature using a spectrometer (Shimadzu, Model UV-2500PC recording spectrophotometer) equipped with a quartz cell of 10 nm optical path length. UV-Vis absorption spectra demonstrate the progress of

the reduction process. The size of core Ag-Pd nanoparticles, which has an average diameter of 3.9 nm and a standard deviation of 1.2 nm, was determined using a transmission electron microscopy (TEM), (JEOL, Model JEM1230) at 80 kV.

2.3. Fabrication of TN-LCDs

Twisted namatic (TN)-LCD cells are fabricated using a NLC, 5CB (K-15, Merck) as a host material doped with Ag-Pd metal nanopatricles that are protected from their aggregation by covering them with NLC, 5CB as a ligand. The concentration of the metal nanometer is 0.1 wt% that gives the volume compaction factor of 1.1×10^{-4}. The thickness of the NLC layer is 5.1 μm.

2.4. Determination of E-O Characteristics and Dielectric Properties of FM-TN-LCD Cells

Electro-optic characteristics of FM-TN-LCD cells were determined with a measuring instrument (Ohtsuka, Model LCD-5200) and an in-house instrument; and the dielectric properties were measured with LCR meters (Hioki, Model 3522–50 and HP, Model 4284 A) together with a software developed by the authors.

3. RESULTS

Figure 1 shows the E-O characteristics called V-T curves, where the frequency of the operating voltages is used as a parameter; the humps occurring just after the threshold voltage are originated from the slightly off situation from the minimum condition for the normally black state. It is shown that the Ag-Pb/5CB system has a long term stability in its EO performance compared to that of the Ag/5CB system. From Figure 1, it is recognized that the threshold voltages increase as decreasing frequency; while, by increasing the frequency above 2 kHz it tends to saturate to have a value that is identical with that of the undoped cell. Using threshold voltage the conventional equation for the threshold voltage of TN-LCDs and the data of Figure 1, we plot the data of $\Delta\varepsilon(f)/\Delta\varepsilon(2\text{kHz})$ and draw a curve in Figure 2, where the solid line is drawn using an approximate formula $\Delta\varepsilon(f)/\Delta\varepsilon(2\text{kHz}) = \exp(-f/f_0)$ with $f_0 = 455$ Hz. This effect may be attributed to the Maxwell-Wagner (M-W) effect for a heterogeneous dielectrics [1–10]. For this reason, we have a motive to investigate the dielectric properties of FM-TN-LCDs in detail.

Figures 3, 4 and 5 show the dielectric and electrical properties of our heterogeneous dielectric medium comprising the NLC host and

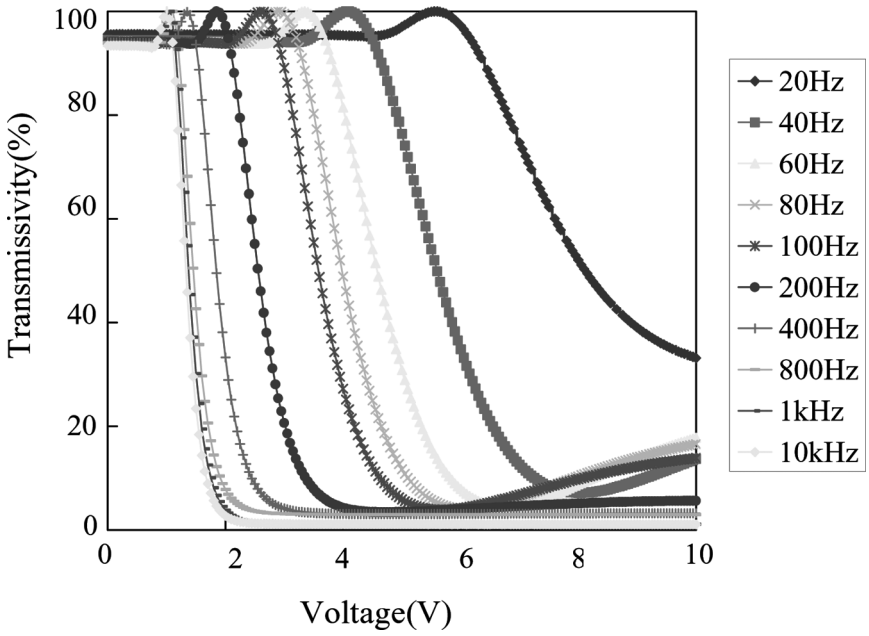

FIGURE 1 V-T curves of a TN-LCD cell with Ag-Pd/5CB, 0.1 wt%; where the frequency is used as a parameter.

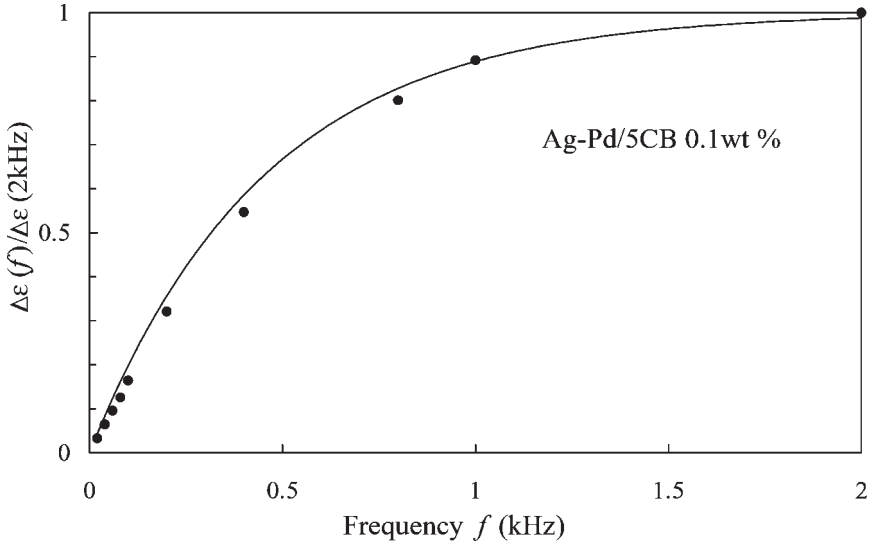

FIGURE 2 Curve of $\Delta\varepsilon(f)/\Delta\varepsilon(2\,\mathrm{kHZ})$, where the solid line is drawn using an approximate formula: $1-\exp(-f/f_0)$ with $f_0 = 455\,\mathrm{Hz}$.

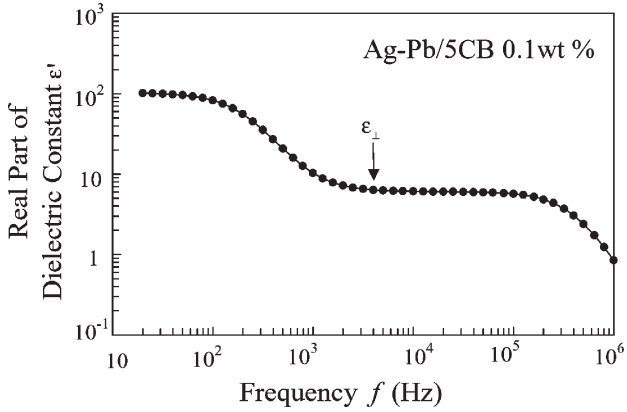

FIGURE 3 Dielectric constant of the TN-LCD cell, ε', at the voltage of below the threshold voltage.

Ag–Pd metal nanoparticles: the results of the frequency dispersion of the dielectric constant ε', its imaginary part ε'', and the electrical conductivity calculated from the equation $\sigma = \varepsilon''\omega$, where all these data are taken for an AC field below the threshold voltage, say at 100 mV; and at the temperature of 25°C. The real part of the dielectric constant, $\varepsilon'(\omega)$, increases from $\varepsilon(\infty)$ to $\varepsilon(0)$ as the frequency decreases below 2 kHz; the imaginary part, $\varepsilon''(\omega)$ gives a relaxation frequency as $f_R = 200$ Hz at which the $\varepsilon''(\omega)$ has a peak value; further the system electrical conductivity $\sigma(\omega) = \varepsilon''(\omega)$. ω is very small, say 10^{-8} S/m at

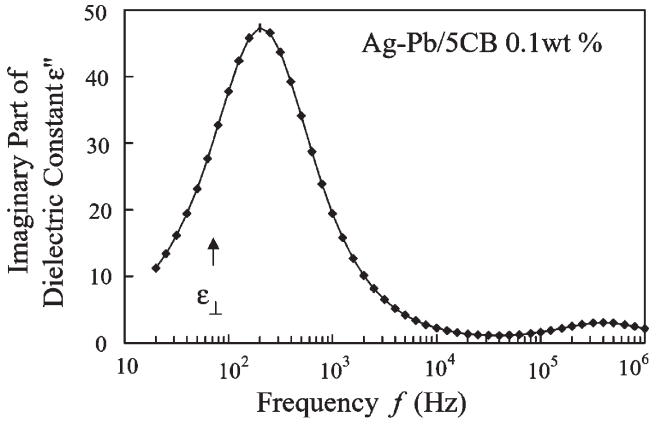

FIGURE 4 Imaginary part of the TN-LCD cell, ε''.

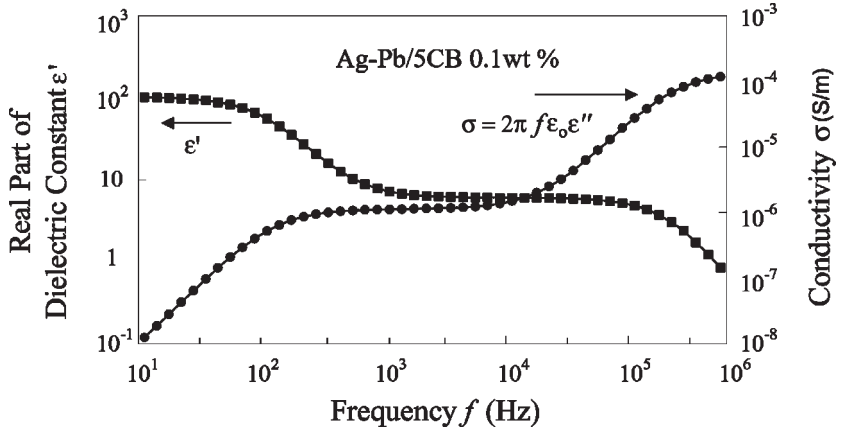

FIGURE 5 Plot of $\sigma(f) = 2\pi f \varepsilon_0 \varepsilon''$ together with $\varepsilon'(f)$.

low frequency, but the $\sigma(\omega)$ increases as increasing the frequency and tends to saturate to a value of 1×10^{-4} S/m above 2 kHz. These phenomena may be attributed to the performance of the FM-TN-LCD fabricated by doping Ag-Pd bimetallic nanoparticles composite, as will be discussed in the next section.

4. ANALYTICAL CONSIDERATION

The obtained phenomena in this research may be numerically analyzed using the conventional Maxwell-Wagner theory that is formulated based on potential theory [7–10] as described in our previous paper [4,5]. However, the traditional theory is unable to demonstrate the fact that the relaxation frequency increases with increasing the concentration of metal nanoparticles, which is actually obtained in the experimental data [4,5]. In order to solve this problem, we have developed an alternative formulation based on a distributed equivalent circuit model together with a crystal model [6]. The concepts of these models are illustrated in Figure 6 and 7. We use this theory to analyze the experimental results.

The relaxation time of a circuit R-C component is $\tau = RC$ and it is also given as $\tau = \varepsilon/\sigma$, where ε and σ being the dielectric constant and the electrical conductivity. Each element shown in Figure 7(c) has individual relaxation time: $\tau_1 = \varepsilon_1/\sigma_1$ for the LC and $\tau_2 = \varepsilon_2/\sigma_2$ for the metal nanoparticle, respectively. In the particular case where τ_1 and τ_2 are not identical, that is, $\tau_1 \neq \tau_2(\varepsilon_1/\sigma_1 \neq \varepsilon_2/\sigma_2)$, then an accumulated oscillating electrical charges $\Delta Q(t)$ appear in the boundary

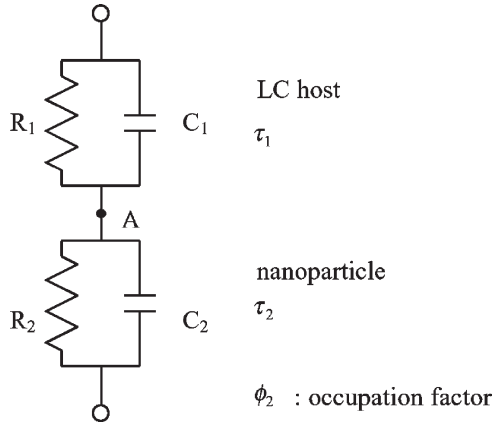

FIGURE 6 Equivalent circuit model of an element comprising of a metal nanoparticle and the neighboring liquid crystal.

between two media that is actually on the surface of the metal nanoparticle corresponding to the point A in Figure 6. In the actual whole system, each element (Fig. 7(c)) participate in forming the series and parallel circuits; and $\Delta Q(t)$ forms a dipole polarization on the metal nanoparticles. After some calculations based on circuit theory, we have an equation of the oscillating charges

$$\Delta Q(t) = \frac{\sigma_1 \sigma_2 \phi_2^{2/3} \quad \Delta\tau}{\sigma_1 \phi_2^{1/3} + \sigma_2 \; 1 + j\omega\tau_0} V \exp(j\omega t), \tag{1}$$

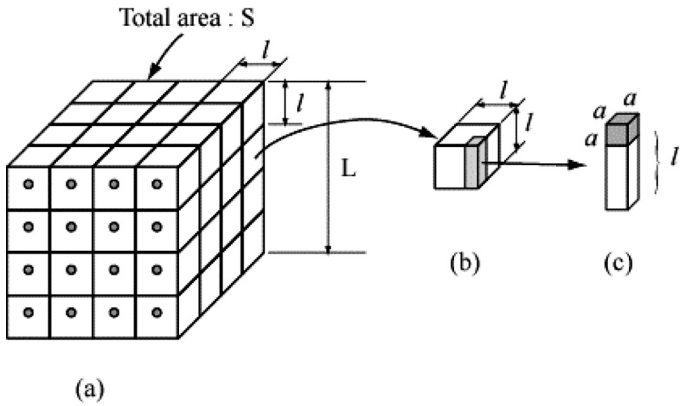

FIGURE 7 Crystal mold of a system of LC and nanopatricles; (a) whole scope, (b) a sub-system, and (c) an element.

where $j = \sqrt{-1}$ and τ_0 is the relaxation time of the system that reads

$$\tau_0 = \frac{\sigma_1 \tau_2 \phi_2^{1/3} + \sigma_2 \tau_1}{\sigma_1 \phi_2^{1/3} + \sigma_2} \tag{2}$$

where ϕ_2 stands for the volume occupation ratio of the metal nanoparticles relative to the whole volume [6]. In our case $\phi_2 = 1.1 \times 10^{-4}$.

The appearance of the oscillating charges on each metal nanoparticle given by Eq. (1) is the origin of the M-W effect, which produces the increase in the dielectric constant of the whole system at low frequency $\omega < 1/\tau_0$, where in this particular case $\tau_0 = 7.96 \times 10^{-4}$ s; and at the same time, the decrease in the electrical conductivity of the whole system at $\omega < 1/\tau_0$; but these variations disappear above $\omega > 1/\tau_0$. These behaviors may be affected by the frequency dependence of the effective conductivity of electrons in the metal nanoparticle as

$$\sigma_2 = \frac{Nq^2\tau_e}{m}\left[1 - \frac{K\Delta\tau}{(1 + j\omega\tau_0)3\varepsilon_0}\right], \tag{3}$$

where $K = \sigma_1\sigma_2\phi_2^{2/3}/(\sigma_1\phi_2^{1/3} + \sigma_2)$. Equation (3) is derived by taking account of the depolarization field originated from the ΔQ.

5. DISCUSSIONS

The frequency dependence of σ_2 given by Eq. (3) are:

For $\omega \to \infty, (\omega\tau_0 > 1)$;

$$\sigma_2(\infty) = \frac{Nq^2\tau_e}{m}; \tag{4}$$

and for $\omega\tau_0 < 1$

$$\sigma_2(0) = \frac{Nq^2\tau_e}{m}[1 - K\Delta\tau]. \tag{5}$$

Thus, $\sigma_2(\infty) > \sigma_2(0)$; this may cause the behavior in the $\sigma^{av}(\omega)$ as shown in Figure 5, where σ^{av} stands for the average value of the whole system.

Regarding τ_0, Eq. (2) is also rewritten as

$$\tau_0 = \tau_1\left[1 - \frac{\sigma_1}{\sigma_2}\frac{\Delta\tau}{\tau_1}\phi_2^{1/3}\right], \tag{6}$$

by assuming that $\sigma_1 << \sigma_2$ and $\Delta\tau/\tau \approx 1$. This equation demonstrates that τ_0 decreases with the increase of ϕ_2 and this trend agree with the experimental data [4,5]. While, the conventional formula for τ is

$$\tau = \frac{2\varepsilon_1 + \varepsilon_2}{2\sigma_1 + \sigma_2}, \tag{7}$$

this equation has no dependence of ϕ_2.

The conventional theory gives the formula for the dielectric strength $\varepsilon(0) - \varepsilon(\infty)$, are given as follows [7–10]:

$$\varepsilon(0) - \varepsilon(\infty) = \frac{9\phi_2(\sigma_2\varepsilon_1 - \sigma_1\varepsilon_2)^2}{(2\varepsilon_1 + \varepsilon_2)(2\sigma_1 + \sigma_2)^2} \approx 9\phi_2\varepsilon_1^2/(2\varepsilon_1 + \varepsilon_2). \tag{8}$$

From our equivalent circuit model, we have

$$\varepsilon(0) - \varepsilon(\infty) = \frac{\varepsilon_1\varepsilon_2\phi_2^{2/3}\Delta\tau}{\varepsilon_2\tau_1 + \varepsilon_1\tau_2\phi_2^{1/3}}. \tag{9}$$

The increase in experimental values of $(\varepsilon(0) - \varepsilon(\infty))/\varepsilon_1$ are $10 \sim 100$; in this case 28.6. In both cases (Eq. (8) and Eq. (9), this increase may be obtained by decreasing the denominators to have the value of $10^{-1} - 10^{-3}$. By using the Drude model: $\varepsilon_2 = 1 - \sigma_2\tau_e/\varepsilon_0$, where τ_e and ε_0 being the electron collision time and the dielectric constant of vacuum; we obtain the value of σ_2 using the conventional theory based on the potential theory (Eq. (8)) as $\sigma_2 = 3.0 \times 10^4\,\mathrm{S/m}$, and from our E-C model (Eq. (9)) $\sigma_2 = 2.5 \times 10^3\,\mathrm{S/m}$, where we set $\tau_e = 3.6 \times 10^{-15}\,\mathrm{s}$ which is 1/13 smaller than that of the Ag of metal crystal due to the finite size effect of the metal nanoparticle, where τ is given as $\tau_e = (\tau_e(d)) = d/\lambda_f$, d and λ_f being the diameter of nanoparticle and the mean free path of the electrons that is about $\lambda_f \approx 50\,nm$ [11]. According to Kawabata and Kubo, the electron collision time in a metal nanoparticle is rather determined by the width of plasmon resonance such that $\tau_e(\Delta\omega_R) = 1/2\Delta\omega_R$ [12]; the value of $\tau_e(\Delta\omega_R) = 2.0 \times 10^{-16}\,\mathrm{s}$ for Ag nanoparticle having the diameter of 4 nm. If we set this value, we obtain $\sigma_2 = 4.4 \times 10^4\,\mathrm{S/m}$ by the EC model; and $\sigma_2 = 6.0 \times 10^5\,\mathrm{S/m}$ by the potential theory. The conductivity of Ag crystal is $\sigma = 6.21 \times 10^7\,\mathrm{S/m}$ and $\tau_e = 4.5 \times 10^{-14}\,\mathrm{s}$ at room temperature [13]; the values obtained in this research are smaller than that of Ag metal by the factor of $1/10^3$ to $1/10^2$. The values σ_2 obtained in this research may be effective ones and may depend on the conditions such as the nature of ligand molecules that are directly close to metal nanoparticles. Our EC model gives a compatibility between τ_0 and $\varepsilon(0) - \varepsilon(\infty)$; therefore the value of σ_2 obtained by the EC model

seems appropriate. Research for exploring the effect of the ligand is now underway and the results will be published elsewhere.

6. CONCLUSIONS

It is shown that TN-LCDs doped with metal nanopatricles such as Ag, Pd, Ag–Pd composite, which are protected by ligand molecules such as nematic liquid crystal, 5CB, exhibit frequency modulation electro–optic (EO) response with short response times of ms or sub–ms order. The devices are called FM-LCDs. Among them the system using Ag-Pd nanoparticles shows long term stability. This the unique EO characteristics of FM-LCDs may be attributed to the Maxwell–Wagner effect of heterogeneous dielectrics that gives rise to the frequency dependence of the dielectric anisotropy. The frequency range of the FM effect is shown to be coincidence with that of the dielectric dispersion and from the dielectric the effective electrical conductivity of the Ag nanoparticle with the diameter of 4 nm is determined to have a value of about 100 times smaller than that of Ag metal.

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