

Near-Infrared Spectral Emissivity of Cu, Ag, and Au in the Liquid and Solid States at Their Melting Points

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Normal spectral emissivities of liquid and solid Cu, Ag, and Au have been determined at their melting points over a wavelength range 1000 to 2500 nm using an apparatus that consists of a cold crucible and a diffraction grating spectrometer. For the noble metals, the emissivities of liquid phases are systematically larger than those of solid phases over the measured wavelength range, and the wavelength dependence of the liquid is similar to that of the solid. The measured emissivities for the liquid metals are compared with those deduced from the optical constants measured by Miller and Krishnan et al. The present results for liquid Cu and Au are in good agreement with the data of Krishnan et al., but not with those of Miller for Cu, which suggests that the optical constants measured by Krishnan et al. for liquid Cu are more accurate than those of Miller. The present data for liquid Ag and Au are in excellent agreement with all previously reported data. For the solid metals at their melting point, a semi-empirical estimation of the emissivity was carried out based upon the Drude model incorporating the effects of interband absorption and a frequency-dependent scattering rate, $\tau^{-1}(\omega) = \tau_0^{-1} + b\omega^2$. The values of τ_0^{-1} and b at the melting point are obtained by fitting the modified Drude model to the measurement results for the solid noble metals.

KEY WORDS: copper; Drude model; electron-phonon scattering; gold; intraband absorption; noble metals; normal spectral emissivity; optical constants; silver.

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1. INTRODUCTION

Normal spectral emissivities of metals at their melting points are of considerable interest, from both practical and scientific points of view. The emissivities of liquid metals at their melting points are often used to determine true temperatures of the melts from the brightness temperatures which can be obtained using radiation thermometers. Therefore, many spectral emissivity data have been reported for metals at their melting points, but most previous data have been confined to the liquid phase. A knowledge of the difference between the emissivities of liquid and solid phases at the same temperature would be important for understanding the behavior of electrons in metals on melting, because the difference in emissivity, as well as other optical properties, is related to that between the electronic structures of the liquid and solid phases. The paucity of data for the solid phase is due to experimental difficulties associated with the increased roughness and deformation of surfaces of solid samples at elevated temperatures. To circumvent this problem, we have measured normal spectral emissivities of liquid and solid Cu [1, 2], Ag [2], Au [2], and Si [3] at their melting points using an apparatus capable of realizing a very smooth surface of the solid sample. However, our previous studies on the noble metals were limited to the visible region.

To our knowledge, there are no experimental data of the spectral emissivity in the near-infrared region for Cu, Ag, and Au at their melting points, except for the emissivity values deduced from the optical constants. In the 1960s, Hodgson [4] and Miller [5] measured the optical constants in the near-infrared region for liquid Ag and those for liquid Cu and Ag, respectively, at their melting points. Their results for liquid Ag are almost identical. In 1990, Krishnan et al. [6] measured the optical constants at 1064 nm for all three noble metals in liquid states at temperatures above the melting point (Cu; 1434 to 1729 K, Ag; 1236 to 1489 K, and Au; 1417 to 1976 K). Since the emissivity values of the liquid metals change linearly and moderately with temperature [6], the emissivities at their melting points can be obtained by extrapolating the data of Krishnan et al. to the melting temperatures. For liquid Ag, the value determined from extrapolation agrees with the data obtained by Miller and Hodgson. However, a significant discrepancy exists between the datum obtained by Krishnan et al. and that by Miller for liquid Cu: the emissivity value of Krishnan et al. is much larger than that of Miller. The discrepancy for liquid Cu cannot be explained in terms of experimental uncertainties that they could recognize and thus reduces the reliability of their results for the optical constants of liquid Cu in the near-infrared region.

For solid Cu, Ag, and Au at their melting points, neither spectral emissivities nor optical constants have been experimentally investigated

in the near-infrared region. However, some theoretical models have been provided to explain the experimental results for near-infrared properties for the metals in solid states at temperatures below their melting points. Near-infrared properties of the noble metals are empirically explained in terms of the Drude formula for a complex dielectric function with a frequency-dependent scattering rate of conduction electrons in the metals. The frequency-dependent scattering rate, $\tau^{-1}(\omega)$, is given by [7–10]

$$\tau^{-1}(\omega) = \tau_0^{-1} + b\omega^2 \quad (1)$$

where ω is the angular frequency of light, τ_0^{-1} is the frequency-independent term, and b is the coefficient of the ω^2 term. All three noble metals possess large absorption peaks in the visible and ultraviolet regions, which are caused by interband transitions between the upper d -band and the Fermi level in the metals. The large interband absorption peaks are considered to affect the complex dielectric function not only in the visible and ultraviolet regions but also in the near-infrared. Taking into account the two effects, Beach and Christy [8] theoretically estimated the spectral reflectivity of Cu, Ag, and Au at room temperature. The feature of the theoretical estimation was their modeling for $\tau^{-1}(\omega)$ in which the scattering rate was made up of three independent components, one due to electron-phonon, one due to electron-electron, and one due to electron-impurity scattering. They considered that the model was capable of representing room-temperature data for the noble metals. However, Parkins et al. [9] have indicated that the model cannot explain the temperature dependence of b , by comparing the predictions of the model with their own experimental results for all three noble metals above and below room temperature. Furthermore, their measured values of b exceed the theoretically estimated values by a factor of 2 or 3. In the model, it is assumed that the quadratic dependence of the scattering rate is entirely due to electron–electron scattering, which is given by Gurzhi’s expression [8]. Smith and Ehrenreich [10] have shown that the assumption is not appropriate for alkali and noble metals at room temperature or higher. They have derived a theoretical model (S-E model) of the form in Eq. (1) for the $\tau^{-1}(\omega)$ due to electron-phonon scattering. Comparing predictions of the two models with experimental data of b for the alkali and noble metals, they have concluded that the electron-phonon scattering mechanism accounts for the quadratic dependence on ω for the metals. According to the S-E model, the coefficient of b is constant at low temperature and increases linearly with T at high temperature. The temperature dependence of b predicted by the S-E model fits well with that observed by Parkins et al. [9] for the three noble metals, although the values of b calculated from the S-E model are also much smaller than those

obtained from experimental data. Recently, it has become well accepted that the frequency dependence of the scattering rate for the noble metals can result from electron-phonon or electron-impurity scattering. A contribution from the electron-impurity scattering, which was not taken into account theoretically, would make all of the measured values larger than predictions of the S-E model.

The purposes of this work are (a) to present reliable data for normal spectral emissivities of Cu, Ag, and Au in liquid and solid states at their melting points in the near-infrared region, (b) to validate previously reported data of the optical constants for the liquid noble metals by means of comparison with the present results, (c) to extend the application of the Drude model with the supplementary effects of interband absorption and the frequency-dependent scattering rate to the emissivity of the noble metals in solid states at their melting points, and (d) to determine values of τ_0^{-1} and b for the solid metals at their melting points by fitting the modified Drude model to the measurement results for the emissivities.

2. MODIFIED DRUDE MODEL

The normal spectral emissivity, $\varepsilon(\lambda)$, of metals is calculated from the optical constants, n and k , via the Fresnel relation and Kirchhoff's law as follows:

$$\varepsilon(\lambda) = 4n/[(n+1)^2 + k^2]. \quad (2)$$

The optical constants are related to the complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, as follows:

$$\varepsilon_1 = n^2 - k^2, \quad \varepsilon_2 = 2nk. \quad (3)$$

According to the Drude theory, the coefficients of the real and imaginary parts of the complex dielectric function are given by

$$\varepsilon_1 = 1 - \omega_p^2/(\omega^2 + 1/\tau^2), \quad \varepsilon_2 = \omega_p^2/[\omega\tau(\omega^2 + 1/\tau^2)] \quad (4)$$

where ω_p is the plasma frequency of the conduction electrons. For noble metals, $\omega\tau \gg 1$ always holds in the near-infrared region and the large interband absorption peaks have a significant effect on ε_1 . Therefore, Beach and Christy [5] considered that a real constant term $\delta\varepsilon_1$, associated with the absorption peaks at shorter wavelengths, must be added to ε_1 of Eq. (4) in the near-infrared region, so they assume

$$\varepsilon_1 = 1 + \delta\varepsilon_1 - \omega_p^2/\omega^2, \quad \varepsilon_2 = \omega_p^2/(\omega^3\tau). \quad (5)$$

As described above, the scattering rate of the conduction electrons is expressed by the form of Eq. (1). Thus, the normal spectral emissivity of the noble metals in the near-infrared can be estimated from the data for $\delta\varepsilon_1$, ω_p , τ_0^{-1} , and b .

3. EXPERIMENTS

Figure 1 shows the experimental setup for recording the normal spectral radiance emitted from the sample. The setup was essentially the same as that used in our previous studies [1–3]. The purities of the samples used in this study were 99.994 mass% for Cu and 99.99 mass% for Ag and Au. Each sample was machined into a cylinder (20 to 25 mm in diameter and 5 to 25 mm in length). The sample was placed on a graphite plate and heated using the cold crucible. Contact between the sample and the graphite plate did not cause a major problem because of the small solubility of carbon in the liquid noble metals. To avoid surface oxidation of the sample, the sample was heated in a flow of Ar gas deoxidized with Mg ribbons at about 750 K.

When the sample was melted, the diameter of the melt surface was approximately 25 mm. To obtain only the normal radiation from the heated sample, a diaphragm (8 mm in diameter and 20 mm in length) was

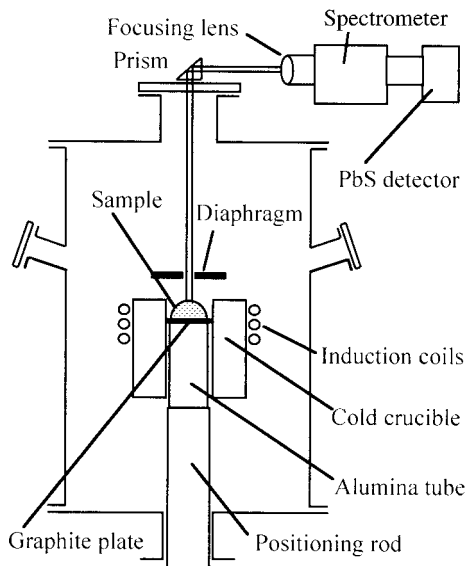


Fig. 1. Schematic diagram of experimental setup.

placed at a distance of approximately 50 mm vertically above the melt surface. After passing the diaphragm, the normal radiation emitted from a circular region of approximately 8 mm in diameter in the center of the sample surface was led to the spectrometer by a combination of a prism and a focusing lens and was measured over the wavelength range 1000 to 2500 nm. The spectrometer (produced by Shimadzu Co., Model SPG-100IR) consists of a diffraction grating monochromator and a PbS detector. The spectrometer was calibrated for converting the output voltage from the detector into the spectral radiance with three fixed-point black-bodies of Ag, Au, and Cu. The calibration procedures are also described in our previous papers [1–3].

A pair of spectral emissivities of the liquid and solid at the melting point at a single wavelength was obtained during one freezing transition of the sample. The measurement on freezing is carried out at intervals of 50 nm in the wavelength range 1000 to 2500 nm. After the emissivity measurements, no oxide film was detected on the resolidified sample surface using electron probe microanalysis. In addition, the root-mean-square roughness of the resolidified sample surface, measured with a profile measurement microscope (produced by Keyence, Model VF-7500), was negligibly small (less than 15 nm).

4. MEASUREMENT RESULTS

Measurement results for normal spectral emissivities of Cu, Ag, and Au at their melting points are plotted as a function of wavelength in Figs. 2a, 3a, and 4a, respectively. Unfilled circles and triangles represent the emissivities measured for liquid and solid phases, respectively. For each metal, sixty-two measurements of a pair of the emissivities at a wavelength were carried out in two independent series, one with an increase of wavelength and the other with a reduction. The upper and lower broken curves on the figures are drawn according to fitted polynomial functions for the measured emissivities of the liquids and solids, respectively. Each function is obtained by a least-squares fitting routine as follows:

$$\varepsilon(\lambda) = \sum_{i=0} M_i \lambda^i \quad (6)$$

where λ is the wavelength in nm and M_i 's are the coefficients given in Table I. Relative standard deviations (RSD) of the experimental data from the fitted values are also listed in Table I. The solid lines on the figures represent the emissivities calculated using the modified Drude model for the solid metals at their melting points. The details of the modeling will be described in Section 5.3.

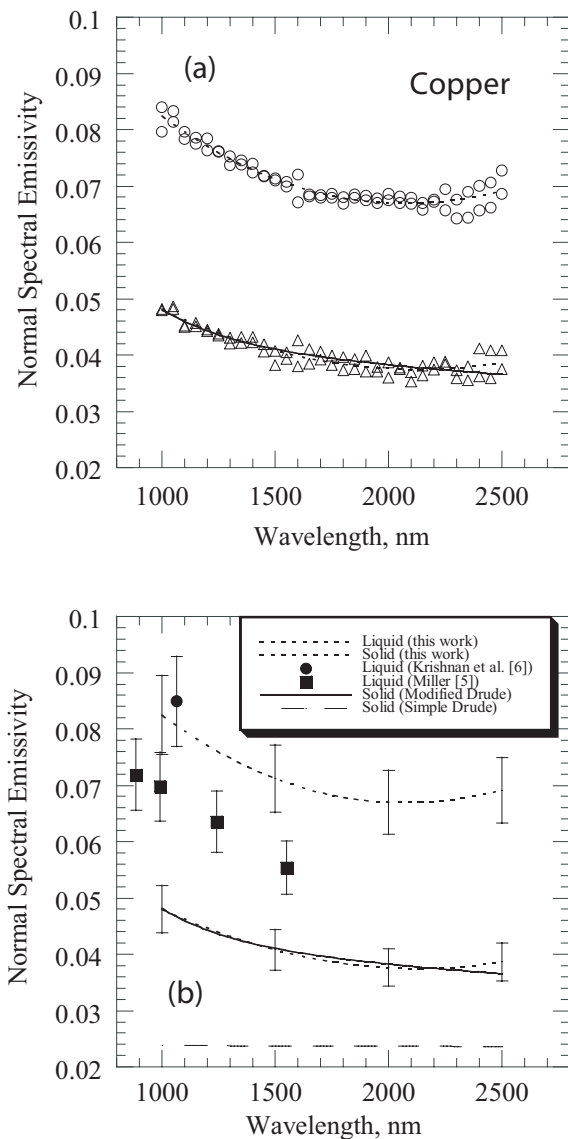


Fig. 2. (a) Measured normal spectral emissivities for liquid and solid Cu at melting point. (b) Comparisons between present and previous experimental emissivity data and the simple and modified Drude models.

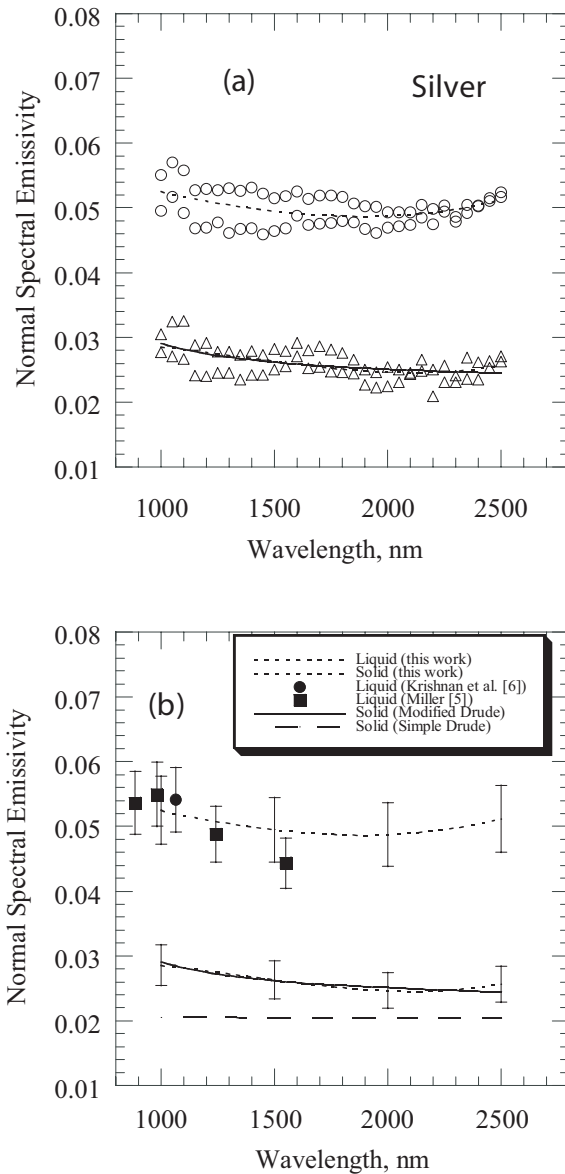


Fig. 3. (a) Measured normal spectral emissivities for liquid and solid Ag at melting point. (b) Comparisons between present and previous experimental emissivity data and the simple and modified Drude models.

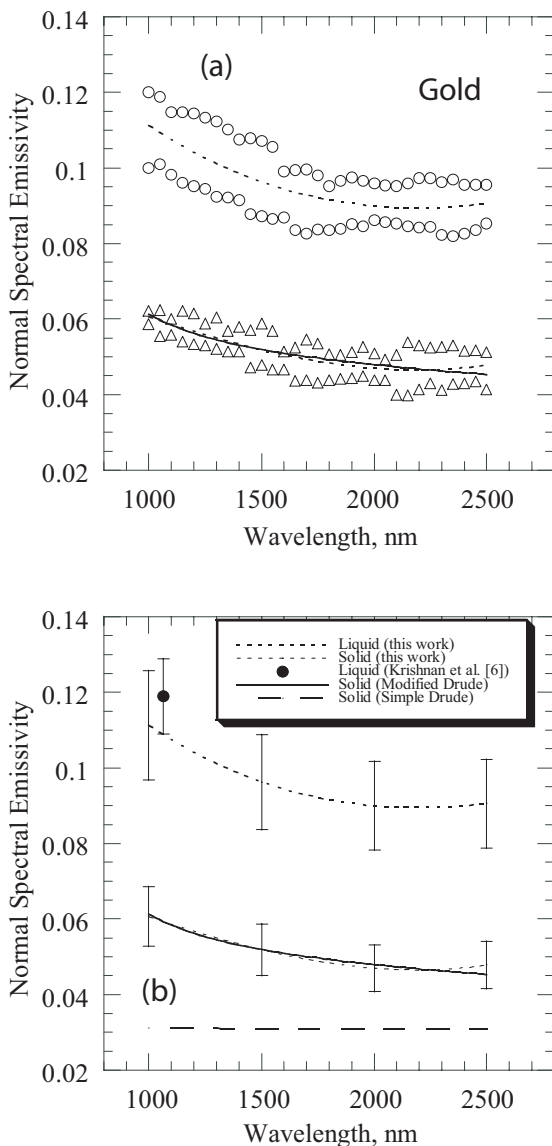


Fig. 4. (a) Measured normal spectral emissivities for liquid and solid Au at melting point. (b) Comparisons between present and previous experimental emissivity data and the simple and modified Drude models.

Table I. Coefficients of M_i in Eq. (6) Obtained by Regression of Measured Emissivity to Polynomial Function and Relative Standard Deviations (RSD) of Measured Data from Fitted Values

M_i	Emissivity of Cu		Emissivity of Ag		Emissivity of Au	
	liquid	solid	liquid	solid	liquid	solid
M_0	1.2874×10^{-1}	7.2981×10^{-2}	6.1307×10^{-2}	2.6146×10^{-2}	1.7414×10^{-1}	8.2448×10^{-2}
M_1	-6.3358×10^{-5}	-3.1514×10^{-5}	-8.7853×10^{-6}	1.1228×10^{-5}	-8.8129×10^{-5}	-2.1087×10^{-5}
M_2	1.7974×10^{-8}	6.0911×10^{-9}	-1.3276×10^{-9}	-1.1667×10^{-8}	2.76×10^{-8}	-3.1473×10^{-9}
M_3	-8.6643×10^{-13}	4.1011×10^{-13}	1.2895×10^{-12}	2.8378×10^{-12}	-2.2886×10^{-12}	2.418×10^{-12}
RSD (%)	1.4	2.6	3.8	5.9	7.8	8.4

For all the noble metals, the emissivities of the liquid are systematically larger than those of the solid at the melting point at all the measured wavelengths. The emissivities of the liquid and solid exhibit a small decrease of emissivity with increasing wavelength, except for the upper end of the wavelength range. The emissivity increase on melting and the negative dependence on wavelength are roughly explained in terms of the equation derived by Grass [11], which is a good approximation of the normal spectral reflectivity deduced from the simple Drude model (Eq. (4)) for the near-infrared region. According to the equation, the normal spectral emissivity is expressed by

$$\varepsilon(\omega) = 1 - R(\omega) = \omega_p^2 / (2\pi\sigma_{dc} \sqrt{\omega_p^2 - \omega^2}) \quad (7)$$

where $R(\omega)$ is the normal spectral reflectivity and σ_{dc} is the dc conductivity in s^{-1} (cgs units). The plasma frequency is defined by

$$\omega_p^2 = 4\pi N_{\text{eff}} e^2 / m \quad (8)$$

where N_{eff} is the effective electron density and m is the free electron mass. Thus, the change in the emissivity on melting can be evaluated using values reported for σ_{dc} and N_{eff} for the liquid and solid noble metals at their melting points. The ratios ($\sigma_{\text{Liquid}}/\sigma_{\text{Solid}}$) of the measured σ_{dc} for the liquid to that for the solid are 0.490, 0.478, and 0.439 for Cu, Ag, and Au, respectively [12]. From the data of de Hass–van Alphen effect, Miller considered that N_{eff} increases by only several percents (Cu: 8%, Ag: 4%, and Au: 7%) on melting [5]. Therefore, the emissivity increase observed on melting is mainly attributed to the relatively large decrease in σ_{dc} caused by the additional disorder in liquid metals.

5. DISCUSSION

5.1. Uncertainty of Emissivity

The uncertainty of the measured emissivity is mainly due to the following three factors: (a) the calibration of the spectrometer, (b) the drift in the sensitivity of the PbS detector, and (c) changes in the geometry of the sample surface caused by the oscillation of the molten sample and the phase transition. Relative values of the individual uncertainties and the combined standard uncertainties of the emissivity are listed in Table II. The relative uncertainties associated with the first factor were estimated based upon the standard deviation of 60 calibration results with the three fixed points of Cu, Ag, and Au, respectively. The relative uncertainties associated with the second factor can also be estimated using the standard deviation of the calibration results, because the uncertainty due to the quality of the fixed-point blackbody was expected to be much less than that for the second factor. Therefore, the relative uncertainties due to the second factor were estimated by interpolating the standard deviations of the calibration results at the three fixed points to the output voltages obtained for the spectral radiation emitted from the sample, since the magnitude of the relative uncertainty depends upon that of the voltage. The relative uncertainties due to the third factor were roughly estimated as the standard deviations of the data points from the fitted values, because neither the roughness nor the macroscopic shape of the sample surface could be measured *in situ* during the phase transition of the sample in this

Table II. Relative Values of Individual Uncertainties and Combined Standard Uncertainties of Emissivity

Uncertainty sources	Relative uncertainties (%)					
	Cu		Ag		Au	
	Liquid	Solid	Liquid	Solid	Liquid	Solid
Calibration of spectrometer	3.4	3.4	5.9	5.9	6.3	6.3
Drift in sensitivity of PbS detector	7.6	7.7	7.8	7.8	7.6	7.7
Change in geometry of sample surface	1.4	2.6	3.8	5.9	7.8	8.4
Relative combined standard uncertainty (%)	8.4	8.8	10	11	13	13

study. It should be noted that the uncertainties due to the third factor were not underestimated, because the data scattering was caused not only by the third factor but also by the second one. The combined standard uncertainties can be estimated from the square root of the sum of the squares of the individual uncertainties.

5.2. Comparison with Emissivity Deduced from Optical Constants

Data for the measured emissivities for the liquid noble metals were compared with those deduced from optical constants measured for liquid Cu and Ag by Miller [5] and those for liquid Cu, Ag, and Au by Krishnan et al. [6] at their melting points. The optical constants obtained by Hodgson [4] for liquid Ag were omitted in the comparison, because they are identical with those of Miller. Our experimental and modeling results and the previous data are displayed for Cu, Ag, and Au in Figs. 2b, 3b, and 4b, respectively. The upper and lower broken lines on the figures indicate the emissivities calculated using Eq. (6) for the liquid and solid, and the filled squares and circles denote the previous data obtained by Miller and Krishnan et al., respectively. The error bars of the broken lines and filled circles correspond to the combined standard uncertainty of the present data and the confidence interval for 95% limits of the data of Krishnan et al., respectively. The error bars of the data of Miller are estimated from the maximum uncertainty (9%) of the optical constants measured by him.

The important results of the comparisons with the emissivities deduced from the optical constants are as follows: (a) good agreement between our results and the data of Krishnan et al. for all three noble metals, and (b) significant deviations between our results and the data of Miller for liquid Cu. These results suggest that our results and the optical constants measured by Krishnan et al. are more reliable than those by Miller for liquid Cu. The emissivities obtained by Miller for liquid Cu are much smaller than our results and the data of Krishnan et al., but are larger than our results for the solid. Therefore, the discrepancy could be due to the possible existence of the solid phase in the measured area of the liquid sample investigated by Miller. For liquid Ag, our results are in excellent agreement with both of the previous data. This agreement confirms the validity of our results for Ag, which showed a relatively large uncertainty of the data.

5.3. Comparison with Modeling of Emissivity

We will discuss the validity of (a) the application of the modified Drude model to the near-infrared emissivities for the noble metals at their

melting points and (b) the values of the parameters used in the emissivity calculations. Each of Figs. 2b, 3b, and 4b shows the respective data sets of the emissivities derived by the modified and simple Drude models for the solid metals at their melting points; the solid and long-dashed lines represent the emissivities calculated using Eqs. (5) and (7), respectively. The parameters ($\delta\epsilon_1$, ω_p , τ_0^{-1} , and b) used in the modified Drude model are listed in Table III. The values of $\delta\epsilon_1$ and ω_p were obtained by extrapolating the data measured by Parkins et al. [9] at three temperatures (77, 295, and 425 K) to the melting point (Cu: 1357.77 K, Ag: 1234.93 K, and Au: 1337.33 K), since there remain fairly large differences between the theoretical and experimental values [9, 10]. The extrapolations were based upon first-order polynomial functions of temperature obtained from least-squares fits to the data at the three different temperatures, because the two parameters exhibit moderate and linear dependence on temperature [9]. After the two extrapolated values were inserted into Eq. (5), the other two values (τ_0^{-1} and b) were determined by fitting Eqs. (1) to (5) to our measured data for the emissivities on the basis of the Levenberg–Marquardt algorithm for the general curve fit. On the other hand, the emissivities for the simple Drude model were deduced from the same extrapolated values of ω_p as that used in the modified Drude model and published data [12] of σ_{dc} for the noble metals in solid states at their melting points.

It can be concluded that the modified Drude model is more suitable for the near-infrared emissivities of the noble metals at their melting points than the simple Drude model, from comparisons between the measurements and modeling results. The simple Drude model predicts that the derivative of the emissivity with respect to wavelength ($d\epsilon/d\lambda$) is almost constant in the near-infrared region. However, the prediction is inconsistent with the steep increase of the magnitude of the measured $d\epsilon/d\lambda$ with decreasing wavelength observed at shorter wavelengths, as shown in Figs. 2b, 3b, and 4b. We can consider that the difference of the measured $d\epsilon/d\lambda$ from that shown by the simple Drude model is mainly due to the quadratic dependence of the scattering rate on frequency, i.e., the effect

Table III. Values of $\delta\epsilon_1$, ω_p , τ_0^{-1} , and b for Estimations of Emissivities for Solid Cu, Ag, and Au at Melting Points

	$\delta\epsilon_1$	ω_p (10^{16} s $^{-1}$)	τ_0^{-1} (10^{13} s $^{-1}$)	b (10^{-18} s)
Solid Cu	3.64	1.29	24.11	11.91
Solid Ag	2.79	1.40	15.70	3.008
Solid Au	3.04	1.27	31.29	15.21

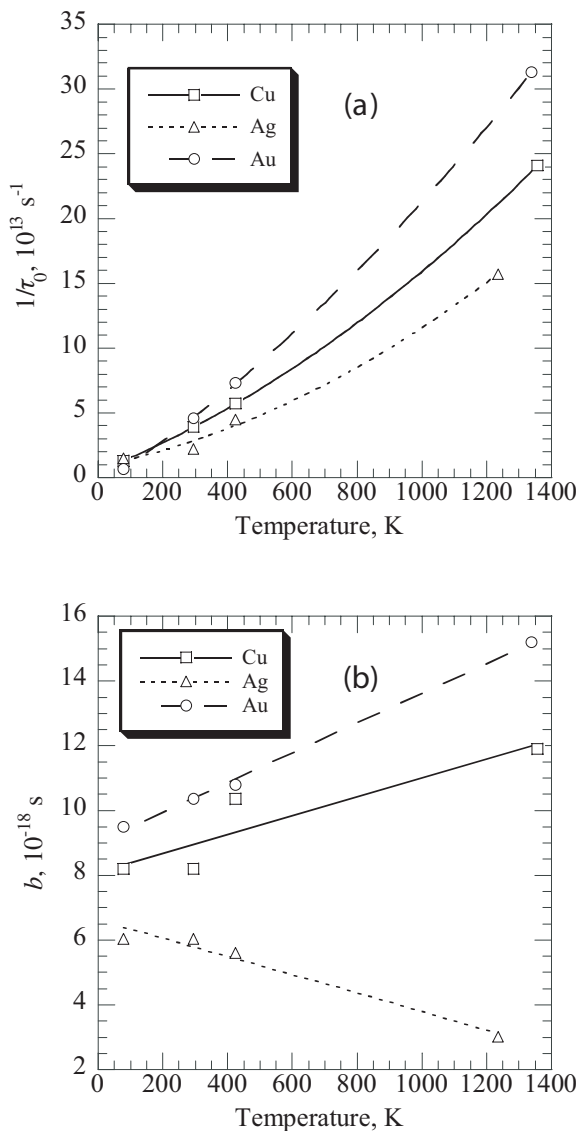


Fig. 5. Temperature dependence of (a) τ_0^{-1} and (b) b ; the values measured by Parkins et al. [9] at 77, 295, and 425 K and the present data at the melting points are plotted as a function of temperature.

of b . In addition, the emissivities of the simple Drude model are much smaller than the measured data. It is difficult to consider that the discrepancy is only due to the possible difference between the value of ω_p used in the model and the true value. A more plausible explanation would seem to be that the effects of $\delta\varepsilon_1$ for the noble metals are maintained at their melting points.

In order to validate the present values of τ_0^{-1} and b for the melting points, they were compared with the reported data at temperatures below the melting point. The data of τ_0^{-1} and b obtained by us for the melting point and by Parkins et al. [9] for 77, 295, and 425 K are plotted as a function of temperature in Figs. 5a and 5b. The lines on Figs. 5a and 5b are drawn according to the second- and first-order polynomial functions, respectively, obtained from least-squares fits to the data at the four different temperatures. Inspection of Fig. 5a indicates that τ_0^{-1} exhibits strong positive dependence on temperature, compared to other three parameters. This result is consistent with previously reported experimental and theoretical results [9, 10]; τ_0^{-1} increases steeply with temperature at high temperatures. However, it is not clear whether the second-order polynomial fits to the data of τ_0^{-1} is reasonable or not, because the temperature dependence is not quantitatively explained. On the other hand, inspection of Fig. 5b indicates that the present data of b agree well with the plausible finding [9, 10] that b varies linearly with temperature. From these comparison results, it may be concluded that the present values of τ_0^{-1} and b are consistent with previously reported experimental and theoretical results.

6. CONCLUSIONS

Normal spectral emissivities of liquid and solid Cu, Ag, and Au at their melting points have been determined in the wavelength range 1000 to 2500 nm. The measured emissivities for the liquid are compared with those deduced from optical constants measured by Miller and by Krishnan et al. The measured emissivities for the solid are compared with the semi-empirical estimation based upon the Drude model with the supplementary effects of interband absorption and a frequency-dependent scattering rate. The main results are given below.

- For all the noble metals, the emissivities of the liquid are systematically larger than those of the solid over the measured wavelength range, and the wavelength dependence of the liquid is similar to that of the solid.
- The present results for liquid Cu are in good agreement with those deduced from the optical constants measured by Krishnan et al., but

not with those by Miller, which suggests that the optical constants of Krishnan et al. for liquid Cu are more accurate than those of Miller.

- The present results for liquid Ag and Au are in good agreement with both sets of previous data.
- The modified Drude model is well fit to the measured emissivities for solid Cu, Ag, and Au at their melting points by using τ_0^{-1} and b as the free parameters.
- The present values of τ_0^{-1} and b for the melting point are consistent with previously reported experimental and theoretical results.

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