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Phase Dependence (Liquid/Solid) of Normal Spectral Emissivities of Noble Metals at Melting Points

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Normal spectral emissivities of liquid and solid Cu, Ag, and Au have been determined at their melting (freezing) points in the visible region using a cold crucible as the heating method. The use of the cold crucible enables the solidification front to be moved on the molten metal surface slowly enough to measure the emissivities of liquid and solid phases separately at the freezing point. Combined standard uncertainties of the spectral emissivities and wavelengths have been estimated. In silver, the spectral emissivity obtained for the liquid is systematically larger than that for the solid over the visible region, which is consistent with the prediction from a classical free-electron model. In copper and gold, the spectral emissivities at wavelengths around their absorption edges do not change for the solid-to-liquid transition. The wavelength range where the emissivity of copper is independent of the phase is unexpectedly broad (the width is greater than 40 nm), which differs significantly from classical experimental studies on the so-called X-point in the emissivity of copper. A qualitative explanation is provided for the difference in the phase dependence (liquid/solid) of the emissivity between copper and gold.

KEY WORDS: copper; gold; interband transitions; melting point; silver; spectral emissivity; visible region; X-point.

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1. INTRODUCTION

It is well known that in almost all cases electronic properties of metals change discontinuously when they melt. Therefore, it is considered that the emissivity of a metal at the melting (freezing) point is dependent not only on the wavelength but also on the phase. However, some previous studies have reported that the spectral emissivities of some metals at a specific wavelength (λ_x) do not change on melting, while for shorter wavelengths the spectral emissivities decrease on melting, whereas for longer wavelengths the spectral emissivities increase on melting. The existence of the spectral emissivity (ε_x) insensitive to the phase transition has been observed for Cu [1, 2] and Au [2–5] in the visible wavelength range and for nine refractory transition metals (Hf, Mo, Nb, Re, Rh, Ta, W, V, and Zr) [6] in the near-infrared region. Such a phenomenon has long been known as the specific case of the so-called X-point [6, 7] in the emissivity of metals, which generally refers to an intersection of spectra of the emissivity for a metal at various temperatures. For copper and gold, it is widely recognized that the X-points are related to opposing effects of the phase change on two optical emission mechanisms, viz., intra- and interband transitions. Namely, at the wavelength of λ_x, the expected increase in the intraband emission on melting compensates for the decrease in the interband emission caused by broadening of the absorption edge due to smearing out of the Fermi-distribution. Therefore, an understanding of the X-point phenomenon is of great interest to develop electronic models of optical properties of liquid metals. In addition, the phenomenon has interesting implications for the development of radiation thermometry, because the melting point of metals can provide a useful high temperature standard for the calibration of radiation thermometers.

Despite the importance of the X-point, there have been few efforts to devise a comprehensive model of this phenomenon. The lack of a model is mainly a result of the lack of reliable experimental data of λ_x and ε_x even for the noble metals. To our knowledge, no experimental study on the X-point for the noble metals has been published since 1961. From the present technical point of view, it can be stated that there may be some shortcomings in the previous measurements. For example, serious errors could be caused by the use of conventional crucibles for containing molten samples. The container would lead to contamination of the sample and stray radiation, which affects the emissivity measurements. Furthermore, the uncertainties of the previous data have not been sufficiently estimated.

In order to circumvent the problems due to the container, containerless techniques have been applied to measurements of emissivities for molten metals, especially for levitation techniques using electromagnetic force [8, 9]. We have also adopted a cold crucible technique, which is a type of containerless method, for measuring emissivities of molten copper [10] and silicon [11]. Compared with electromagnetic levitation techniques, the cold crucible has an advantage of easily controlling the position and temperature of the sample both in liquid and solid states. Therefore, the cold crucible is very useful as a heating instrument for experimental investigations of the phase dependence of the emissivity of metals at the melting point.

In this paper, we report values of normal spectral emissivities for Cu, Ag, and Au in liquid and solid states at their melting points in the visible region, measured with an apparatus that consists of the cold crucible and a spectroscope calibrated with the fixed points of Al, Ag, Cu, and Au. We present the results of the spectral emissivity which is insensitive to the phase change on melting and its wavelength for copper and gold with an estimation of the combined standard uncertainties. Our results for gold agree satisfactorily with previous experimental results, but our results for copper differ significantly from previous studies. In addition, we suggest a qualitative explanation for the difference in the phase dependence of the emissivity between copper and gold.

2. EXPERIMENTAL

In the present work, the normal spectral emissivity of the metals was calculated using the following equation:

$$\varepsilon(\lambda) = R_{\mathrm{S}}(\lambda)/R_{\mathrm{B}}(\lambda) \tag{1}$$

where $\varepsilon(\lambda)$ is the normal spectral emissivity, $R_{\mathrm{S}}(\lambda)$ is the normal spectral radiance emitted from the sample, and $R_{\mathrm{B}}(\lambda)$ is the normal spectral radiance emitted from a blackbody cavity at the same temperature as the sample. Values of $R_{\mathrm{S}}(\lambda)$ at the freezing point, T_{f}, were measured with a spectroscope (produced by Shimadzu Co., Model SPG 100S) consisting of a grating monochromator and a photomultiplier tube. To evaluate the normal spectral radiance from the output of the spectroscope, the spectroscope was calibrated with four fixed-point blackbodies of Al, Ag, Au, and Cu. To avoid a systematic error caused by the difference in optical geometry between the calibration and measurement, the calibration was carried out using the same experimental setup as that used in the measurement.

Figure 1 shows the experimental setup, which consists of the spectroscope to measure the normal spectral radiance and a cold crucible to heat the sample. This setup is almost the same as that used in our previous studies [10, 11]. The cold crucible was used with a 20 kW radio-frequency

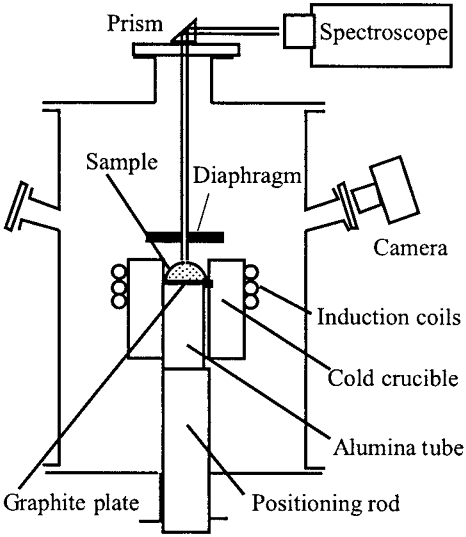

Fig. 1. Schematic diagram of the experimental setup.

(100 kHz) generator to heat samples inductively and to hold the melts by electromagnetic force. Samples of Cu, Ag, and Au were placed on a graphite plate in the cold crucible. Instead of the sample, the fixed-point blackbody was heated on the plate during the calibration with the melting or freezing plateau. Details of the calibration procedure were reported in our previous paper [10]. Values of $R_B(\lambda)$ at T_f were calculated from the Planck radiation law and the ITS-90 values of T_f of Cu (1357.77 K), Ag (1234.93 K), and Au (1337.33 K).

Each sample was cut into a cylinder (20 to 25 mm in diameter and 5 to 25 mm in length), the purity of which was 99.994 mass% for Cu, and 99.99 mass% for Ag and Au. The thermal radiation from the sample perpendicular to its surface was introduced into the monochromator of the spectroscope and, in turn, monochromatic light was introduced into the photomultiplier tube. To avoid surface oxidation, the sample was heated in a flow of Ar gas deoxidized with Mg ribbons at about 750 K.

Both values of $R_S(\lambda)$ for liquid and solid phases at T_f were obtained during one freezing transition by the following procedure. At first, the sample was completely melted in the cold crucible and became hemispherically shaped; then the molten sample was cooled and was moderately resolidified by reducing the power of the generator. Figure 2 shows a typical variation in the signal for copper with time for a wavelength of

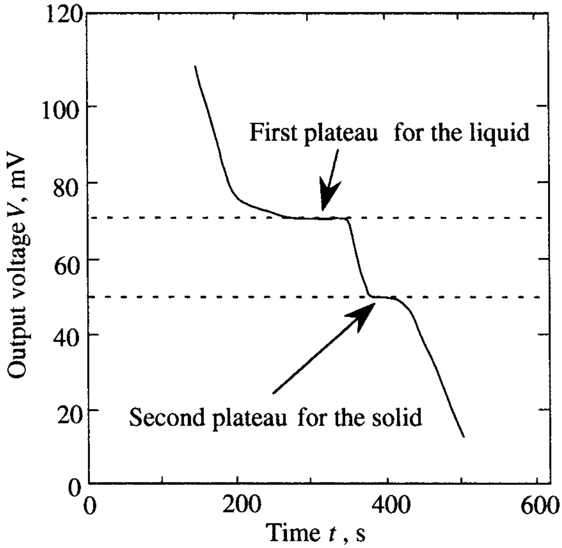

Fig. 2. Typical variation in the signal for Cu with time for a wavelength of 650 nm during the cooling cycle.

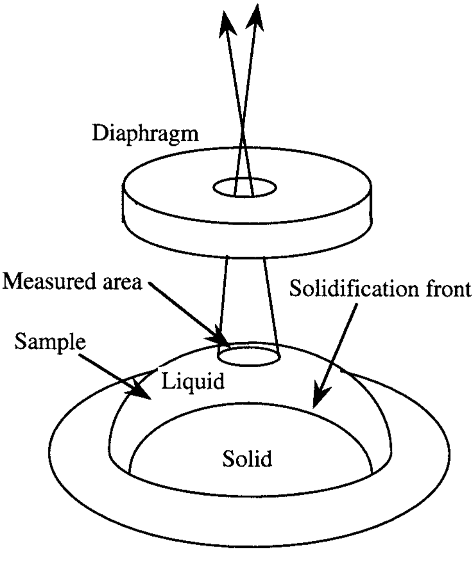

Fig. 3. Schematic view of the sample surface on the early stage of the solidification transition corresponding to the first plateau.

650 nm during the cooling cycle. The first and second plateaus of the signal correspond to the values of $R_S(\lambda)$ for liquid and solid copper at T_f, respectively. Figure 3 shows a schematic view of the sample surface on the early stage of the solidification transition corresponding to the first plateau. In this stage, the value of $R_S(\lambda)$ for the liquid was measured, because the liquid phase still covered the measured area of the sample surface. On the other hand, the value of $R_S(\lambda)$ for the solid was measured after the solid phase spread completely over the measured area. The output signal for $R_S(\lambda)$ at each wavelength was recorded throughout the cooling cycle of the sample. The measurement was repeated at wavelength intervals of 50 or 25 nm.

3. RESULTS

3.1. Normal Spectral Emissivities of Liquid and Solid Cu, Ag, and Au at Melting Points

Table I gives the experimental results of the emissivity for Cu, Ag, and Au in liquid and solid states at T_f. Each emissivity value is expressed as an average from three values of the measured emissivity. The agreement of the three measurements is well within the combined standard uncertainty of the measured emissivity, the estimation of which will be described later. Figures 4 through 6 show the normal spectral emissivity as a function of the wavelength, obtained in the present and previous studies on Cu [1, 2, 12],

Table I. Results of Normal Spectral Emissivities of Cu, Ag, and Au in Liquid and Solid States at Their Melting Points

	Emissivity of Cu		Emissivity of Ag		Emissivity of Au	
Wavelength (nm)	solid	liquid	solid	liquid	solid	liquid
450	0.434	0.434			0.593	0.544
475	0.417	0.417			0.569	0.511
500	0.410	0.410	0.0490	0.0924	0.521	0.501
525	0.382	0.386			0.459	0.469
550	0.333	0.341	0.0415	0.0866	0.369	0.423
600	0.210	0.237	0.0403	0.0741	0.220	0.319
650	0.120	0.163	0.0366	0.0661	0.146	0.239
700	0.0896	0.125	0.0331	0.0595	0.109	0.182
750	0.0741	0.107	0.0311	0.0573	0.0868	0.157
800	0.0628	0.0924	0.0303	0.0552	0.0708	0.138
850	0.0519	0.0796	0.0306	0.0546	0.0576	0.111

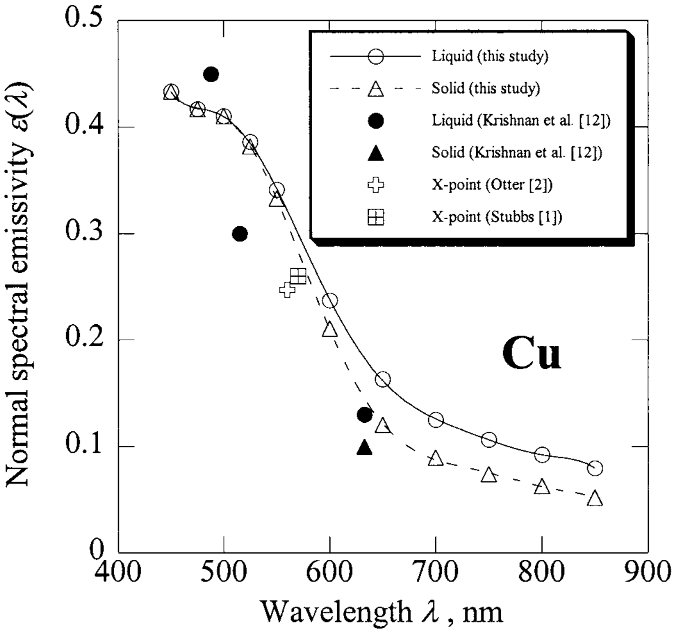

Fig. 4. Normal spectral emissivity of liquid and solid Cu at the melting point as a function of wavelength.

Ag [12], and Au [2–5, 12]. Open circles and triangles represent the average emissivities for liquid and solid phases at T_f, respectively. Comparison between the present and previously published data will be discussed later. The solid and dashed curves on the figures are drawn according to fitting polynomial functions for the emissivities of the liquids and solids, respectively, for which the functions have been obtained by regression of the average emissivities to the following expression:

$$\varepsilon(\lambda) = \sum_{i=0} M_i \lambda^i \tag{2}$$

where λ is the wavelength in nm and M_i is the coefficient given in Table II. It should be noted that the fitting function is available only in the measured wavelength range 450 to 850 nm for Cu and Au and 500 to 850 nm for Ag, because the fitting function is not based upon a theory of optical emission mechanisms. No emissivity value could be determined outside the above ranges because of extremely low S/N ratio of the output.

3.2. X-Points for Cu and Au and Increase in Emissivity of Ag on Melting

The wavelength for an X-point and the normal spectral emissivity at an X-point (λ_x and ε_x), as well as their uncertainties, were determined in the following manner. First, the emissivity measurements at intervals of 50 nm led to an estimation of the wavelength range where an X-point could exist. Secondly, the measurement of $R_S(\lambda)$ on freezing was carried out at intervals of 1 nm in the above range. The value of λ_x was determined as the operating wavelength where only one plateau of $R_S(\lambda)$ occurred throughout the whole process of freezing. The combined standard uncertainty of λ_x has been estimated to be 2.8 nm, from the square root of the sum of the squares of the following uncertainties: (1) the uncertainty associated with the resolution of the monochromator (2.3 nm), (2) the uncertainty associated with the calibration for determining wavelengths (1.5 nm), and (3) the uncertainty associated with the repeatability of determinations of a wavelength (0.3 nm). On the other hand, the value of ε_x is determined as an arithmetic mean of values obtained by substituting the measured value of λ_x for λ in Eq. (2) for liquid and solid phases. The combined standard uncertainty of ε_x is then obtained from the square root of the sum of the

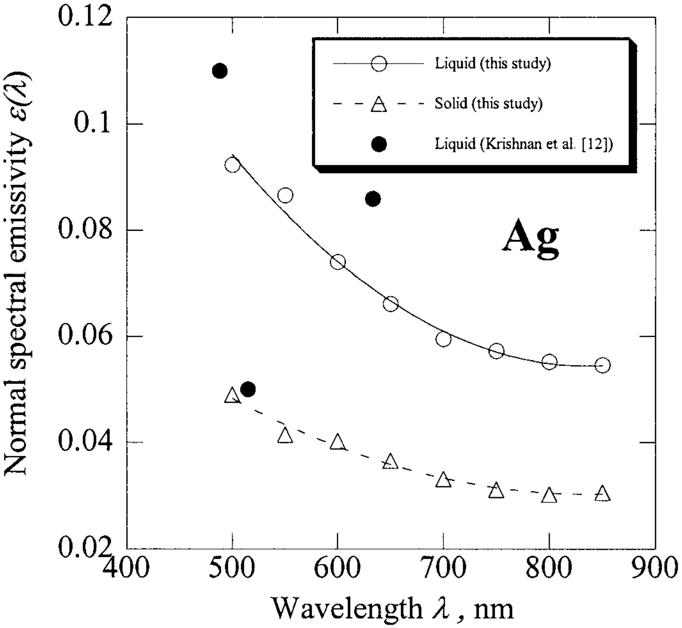

Fig. 5. Normal spectral emissivity of liquid and solid Ag at the melting point as a function of wavelength.

squares of the estimated uncertainties of the emissivities for the liquid and solid phases, as will be reported later.

Inspection of Fig. 4 indicates that normal spectral emissivities of liquid and solid copper are identical over a wavelength range, not at a single wavelength. For copper, the measurement at intervals of 1 nm was made from 450 to 500 nm and only one plateau of $R_S(\lambda)$ was observed at wavelengths below 506 nm. The value of ε_x at the upper limit of λ_x (506 nm) is estimated as 0.405 with a combined standard uncertainty of 0.024. This phenomenon would exist at wavelengths below 450 nm, since the wavelength of 450 nm was just the lower limit of the measurable wavelength range for the spectroscope used in the present work. Inspection of Fig. 6 indicates that for gold there is a typical X-point over the wavelength range investigated. The appearance of a typical X-point for gold in the visible region is consistent with previously reported results [2–5]. For gold, the measurement at intervals of 1 nm was made from 500 to 525 nm and only one plateau of $R_S(\lambda)$ was observed at two wavelengths of 516 and 517 nm. The values of ε_x at the lower and upper limits of λ_x (516 and 517 nm) are

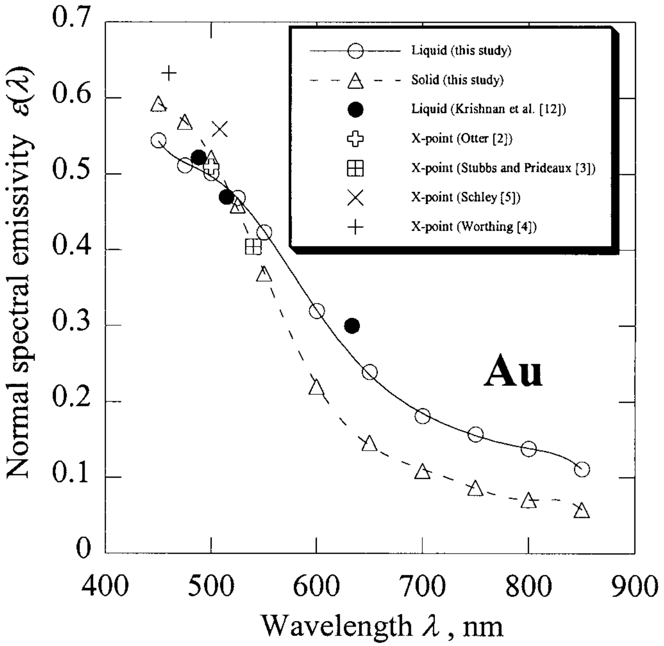

Fig. 6. Normal pectral emissivity of liquid and solid Au at the melting point as a function of wavelength.

Table II. Coefficients of M_i in Eq. (2) obtained by Regression of the Average Emissivity to the Polynomial Function

	Emissivity of Cu		Emissivity of Ag		Emissivity of Au	
M_i	solid	liquid	solid	liquid	solid	liquid
M_0	1263.7	1141.8	0.14112	0.30163	1229.0	955.28
M_1	−13.965	−12.705	-2.6468×10^{-4}	-5.9135×10^{-4}	−14.192	−10.597
M_2	6.5354×10^{-2}	5.9924×10^{-2}	1.5807×10^{-7}	3.5362×10^{-7}	6.9366×10^{-2}	4.9881×10^{-2}
M_3	-1.6788×10^{-4}	-1.5527×10^{-4}			-1.8596×10^{-4}	-1.2913×10^{-4}
M_4	2.5576×10^{-7}	2.3884×10^{-7}			2.9541×10^{-7}	1.9865×10^{-7}
M_5	-2.3127×10^{-10}	-2.1824×10^{-10}			-2.7829×10^{-10}	-1.8174×10^{-10}
M_6	1.1501×10^{-13}	1.0976×10^{-13}			1.4406×10^{-13}	9.1626×10^{-14}
M_7	-2.4285×10^{-17}	-2.3459×10^{-17}			-3.1637×10^{-17}	-1.9653×10^{-17}

estimated as 0.481 (0.026) and 0.479 (0.026), respectively, where the values in parentheses are the combined standard uncertainties of ε_x.

Inspection of Fig. 5 indicates that the normal spectral emissivity of liquid silver at T_f is systematically larger than that of the solid in the visible region. The emissivity increase on melting is somewhat expected based upon a free-electron model of metals, although there are no experimental data in the literature for changes in the emissivity of silver at the phase transition. In silver, the threshold energy (about 4 eV) for interband transitions is much greater than for visible light energy (1.5 to 3.1 eV). Therefore, the phase dependence of the visible emissivity of silver can be qualitatively explained in terms of the Hagen–Rubens relation, which is a simplified formula derived from the Drude model together with the Fresnel equations. According to the relation, the spectral emissivity of metals increases as the electrical resistivity increases when they melt. The resistivity increase is consistent with the additional disorder in liquid metals. This explanation is consistent with the emissivity increase for Cu and Au obtained at longer wavelengths on the assumption that the surface measured in the solid is smooth enough to neglect the effect of the surface roughness on the emissivity.

4. DISCUSSION

4.1. Uncertainty of Emissivity

The uncertainty of the measured emissivity stems from the measurement of $R_S(\lambda)$, the determination of T_f, and the surface condition of the sample. In the present work, the uncertainty of the measured $R_S(\lambda)$ is the dominant component of uncertainty and is estimated as the standard uncertainty of the measured emissivity. The uncertainty associated with the temperature determination is neglected in the uncertainty estimation, because the sample temperature of T_f was directly determined by means of the observation of the freezing plateau. The uncertainty arising from the surface roughness of the sample is also negligible, because the root-mean-square roughness of the surface of the resolidified sample was less than 15 nm; the surface roughness was measured using a profile measurement microscope (produced by Keyence, Model VF-7500). In addition, it was confirmed from the observation by electron probe microanalysis that there was no oxide film on the surface of the resolidified samples.

The uncertainty of $\varepsilon(\lambda)$, which corresponds to that of $R_S(\lambda)$, is caused by the following two factors: (1) random effects due to the difference in macroscopic shape of the sample surface and the electronic noise of the detector of the spectroscope and (2) systematic effects due to the drift in the sensitivity of the detector. The standard uncertainty associated with random effects has been determined both the solid and liquid from the experimental standard deviation in values of $R_S(\lambda)$ obtained in 36 different runs. As a result, the relative value of the standard uncertainty due to the first factor is estimated to be 4.0 and 3.3% for solid and liquid Cu, 10 and 11% for solid and liquid Ag, and 3.6 and 2.8% for solid and liquid Au. On the other hand, the relative value of the standard uncertainty due to the second factor has been estimated to be 2.0%, based upon 15 repeated determinations of the fixed-point blackbody radiance of copper at T_f. The combined standard uncertainty is obtained from the square root of the sum of the squares of the individual standard uncertainties. Thus, the relative value of the combined standard uncertainty is estimated to be 4.5 and 3.9% for solid and liquid Cu, 10 and 11% for solid and liquid Ag, and 4.1 and 3.4% for solid and liquid Au.

4.2. Comparison with Previously Reported Results

There have been a considerable number of experimental investigations for the spectral emissivity of Cu, Ag, and Au in liquid and solid states in the visible region. However, fairly large discrepancies can be seen in the previously reported data. From a technical point of view, the data obtained by Krishnan et al. [12] for liquid and solid Cu and liquid Ag and Au are considered to be the most accurate among the published values. This is because the data by Krishnan et al. have been obtained with a reliable apparatus based upon an electromagnetic levitation technique and rotating analyzer ellipsometry. The levitation technique can eliminate the experimental uncertainty caused by the contact material, and the emissivity measurement by ellipsometry is theoretically superior to other conventional methods since it yields two independent quantities, refractive index (n) and extinction coefficient (k), of which the emissivity is a function. Therefore, the present results are first compared with the data by Krishnan et al. to assess the validity of the present measurements.

Filled circles and triangles shown in Figs. 4 through 6 denote the emissivity measured by Krishnan et al. for the liquids and solid, respectively. It must be emphasized that the present data for liquid Au are in good agreement with those by Krishnan et al. This suggests that the measuring instrument and reference standards used in this work have no significant drawback. For copper and silver, agreement between the present data and those by Krishnan et al. is a little worse. Therefore, it should be stated that there could be a significant uncertainty in the data by Krishnan et al., especially for Ag, because the wavelength dependence for liquid silver reported by Krishnan et al. is not consistent with the dependence expected from the Drude theory. According to this theory, emissivity spectra for metals exhibit negative wavelength dependence over the wavelength range where there is no absorption associated with the interband transition. The present results on the X-point for copper and gold can not be directly compared with the data obtained by Krishnan et al., because their reported data are limited only to the liquid, except for the data on copper at 633 nm.

Figure 6 shows that our results of λ_x and ε_x for gold are in good agreement with those reported by Otter [2] and by Stubbs and Prideaux [3]. In particular, the agreement with the data by Otter demonstrates the validity of our results on gold, because his data are considered to be the most accurate among the previous results, since they were measured with an ellipsometer and without a conventional crucible. On the other hand, there is a significant difference between the present and previous results on the X-point for Cu. The results obtained by Stubbs [1] and Otter [2] indicate that the solid and liquid phases have the same value of emissivity at a single distinct wavelength but not over a wavelength range. It is very difficult to give a quantitative explanation to this discrepancy, because it is impossible to know the details of the previous experiments and to reevaluate the experimental uncertainty. However, the discrepancy could arise from experimental errors in the previous results, which have been eliminated or reduced by the use of the cold crucible or the direct determination of λ_x in the present work. In contrast to our study, the previous results for copper indicate that the spectral emissivities at wavelengths below λ_x increase on freezing. The increase in the emissivity at lower wavelengths could be related to the surface roughness of the solid sample used in the previous studies. It is considered that the surface roughness of our sample is smoother than those in the previous experiments, because a very smooth surface of the sample was realized during the solidification process using the cold crucible. In addition, our method for determining λ_x is considered to be more reliable, because the value of λ_x has been directly determined by comparison of the spectral radiance emitted from the two different phases at the same temperature obtained during an identical run. From these merits of our experiments and the uncertainty analysis, it is expected that our results are more accurate than those of previous studies.

4.3. Insensitivity of Emissivity of Cu and Au to the Phase Change on Melting

The important findings in this study are as follows: (1) a wide wavelength range where the emissivity of copper is insensitive to the phase change on melting and (2) a narrow wavelength range where the emissivity of gold is insensitive to the phase change. These findings lead to a question of why there is a significant difference in the width of the wavelength range for the insensitivity between the two metals whose electronic structures are very similar to each other. We discuss below the difference between the two monovalent noble metals.

In copper, the absorption edge exists at approximately 560 nm, corresponding to a light energy of 2.2 eV. The edge is attributed to the interband transition between the upper d-band and the Fermi surface, $L_3(Q_+)-E_f(L'_2)$, where the band nomenclature is adopted from Mueller and Philips [13]. Since the measured λ_x for copper is shorter than that of the absorption edge, the optical emission at wavelengths of λ_x (below 506 nm) is primarily caused by the interband transition; the contribution of intraband transitions to the emission can be neglected. The interband transition, $L_3(Q_-)-E_f(L'_2)$, also affects the optical emission at λ_x, because the onset of the transition is located at 490 nm [14]. Therefore, by assuming that the emission due to the two transitions near the L-symmetry point is insensitive to the phase change on melting, we can explain the occurrence of the wide wavelength range where the emissivity does not change on melting. This assumption is supported by the experimental work of Miller [15]; his results on the imaginary part of the dielectric constant of liquid Cu, Ag, and Au imply that the absorption edge due to the L transition is rather little affected by the melting transition.

In gold, the absorption edge exists at approximately 500 nm, corresponding to a light energy of 2.5 eV. Unlike copper, the absorption edge is attributed not only to the transition, $L_3(Q_+)-E_f(L'_2)$, but also to the transition [16] between band 5 and band 6 (at E_f) near the X-symmetry point, and the transition [14], $L_3(Q_-)-E_f(L'_2)$, occurs at the wavelength in the ultra-violet region (about 390 nm). The threshold energies for L and X transitions associated with the edge have been estimated to be 2.54 and

1.94 eV, respectively [16]. Because of the existence of the *X* transition, the absorption edge possesses a long nearly exponential tail which extends well above 600 nm, in contrast with the steep edge characteristics of *L* transitions. Therefore, it should be noticed that the insensitivity of the emissivity occurs at wavelengths where the tailing of the absorption edge exists. From these facts, it can be stated that the occurrence of the typical X-point is largely attributed to the sensitivity of the *X* transition to the phase change on melting. Several authors indicate that the *X* transition is more sensitive to the phase change on melting than the *L* transition. Thèye [17] has found that the intensity of the absorption due to the *X* transition strongly depends on microscopic structures of gold film samples. Pells and Shiga [18] have found that the temperature dependence of the absorption intensity for the X transition is strong when compared with the main absorption of the edge. Therefore, we suggest that the absence of the *L* transitions would result in the narrow wavelength range where the emissivity of gold does not change on melting.

5. CONCLUSIONS

Normal spectral emissivities of liquid and solid Cu, Ag, and Au at their melting points have been determined as functions of wavelength in the visible region by means of an apparatus that consists of a cold crucible and a spectroscope. The main results are given below.

- The normal spectral emissivity of Cu does not change during the solid-to-liquid transition at wavelengths below 506 nm, and the emissivity at 506 nm is 0.405 with a combined standard uncertainty of 0.024.
- The normal spectral emissivity of Au does not change during the solid-to-liquid transition over a wavelength range of 516 to 517 nm, and the respective emissivities at 516 and 517 nm are 0.481 and 0.479 with a combined standard uncertainty of 0.026.
- The normal spectral emissivity of Ag in the liquid state is systematically larger than that in the solid state in a wavelength range 500 to 850 nm.
- The difference in the phase dependence of the emissivity between Cu and Au could be caused by the difference in the sensitivity to the phase change on melting between the interband transitions near *X* and *L*-symmetry points in the metals.

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REFERENCES

1. C. M. Stubbs, *Proc. R. Soc. London A* **88**:195 (1913).
2. M. Otter, *Z. Phys.* **161**:539 (1961).
3. C. M. Stubbs and E. B. R. Prideaux, *Proc. R. Soc. London A* **87**:451 (1912).
4. A. G. Worthing, *Phys. Rev.* **28**:174 (1926).
5. U. Schley, *Naturwiss.* **47**:222 (1960).
6. C. Ronchi, J. P. Hiernaut, and G. J. Hyland, *Metrologia* **29**:261 (1992).
7. D. J. Price, *Proc. R. Soc. London* **59**:131 (1947).
8. S. Krishnan and P. C. Nordine, *J. Appl. Phys.* **80**:1735 (1996).
9. J. A. Treverton and J. L. Margrave, *J. Chem. Thermodynamics* **3**:473 (1971).
10. H. Watanabe, M. Susa, and K. Nagata, *Metall. Mater. Trans. A.* **28**:2507 (1997).
11. H. Watanabe, M. Susa, H. Fukuyama, and K. Nagata, *High Temp.-High Press.* **31**:587 (1999).
12. S. Krishnan, G. P. Hansen, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.* **26**:143 (1990).
13. F. M. Mueller and J. C. Philips, *Phys. Rev.* **157**:600 (1967).
14. M. Welkowsky and R. Braunstein, *Solid State Commun.* **9**:2139 (1971).
15. J. C. Miller, *Phil. Mag.* **20**:1115 (1969).
16. M. Guerrisi and R. Rosei, *Phys. Rev. B* **12**:557 (1975).
17. M.-L. Thèye, *Phys. Rev. B* **2**:3060 (1970).
18. G. P. Pells and M. Shiga, *J. Phys. C* **2**:1835 (1969).