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Photoluminescence of gold, copper and niobium as a function of temperature

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ABSTRACT

A specially constructed instrument for measuring the low intensity photoluminescence emission spectra of metals is described. It uses low luminescence optical components and dedicated sample mounting techniques. Room temperature measurements agree closely with literature spectra for high-purity gold and are found to be sensitive to 100 ppm impurities. Detailed spectra are presented, which are weakly temperature dependent, for gold, copper and unpolished niobium between room temperature and 100 K. We conclude that this work provides accurate luminescence data for Au from 300 K down to 100 K. Although the (variable temperature) luminescence data for Cu are consistent both with the room temperature experimental data in the literature and theory, we conclude the role of surface adsorbates and/or oxides cannot be ruled out. Theory suggests that Nb has a factor ~50 lower luminescence intensity than Au and Cu because the real part of the refractive index is a factor ~5 higher and the density of states ~2 eV below the Fermi energy is a factor of ~4 lower than Au and Cu. Measurements are presented for unpolished Nb, but given the lack of signal detection for polished Nb and that theory predicts very weak signals, we conclude that the luminescence signals from pure Nb still remain below the sensitivity of our instrument.

1. Introduction

Over the last decade, it has become clear that Fermi liquid theory (the standard text-book model) cannot explain the properties of an increasing number of metals [1]. We are interested in studying the properties of metals that become superconducting. There is increasing evidence that in many of these metals, the ground state of the conduction electrons and its excitations will require a non-Fermi liquid theory for an accurate description. Also the fundamental mechanism that causes super-conductivity in the high-temperature superconductors remains unknown [2]. Historically, optical measurements have provided essential information about the electronic structure of materials [3–5]. Inelastic luminescence experiments are particularly useful because of the information they provide about occupied and unoccupied states near the Fermi energy. Luminescence studies of metals are not widespread because of the demands of measuring the weak emission [6] with a typical efficiency of 10^{-10}. Theoretical work on the photoluminescence of gold and copper attributes the emission spectrum to radiative transitions between the overlapping d and sp-bands that are close to the Fermi energy [6–8]. The intensity of the photoluminescence emission from metals is weak because of the non-radiative Auger processes that directly compete with the radiative recombination processes [8].

Experimental photoluminescence emission studies for gold, copper and copper–gold alloys at room temperature and some specific low temperatures have been reported previously [6,7]. There has also been work on gold, silver and copper using multi-photon excitation techniques [7].

In this work, we report detailed variable temperature measurements on gold, copper and niobium. In Section 2, the design of the equipment developed for very low intensity photolumines-cence measurements is outlined and discussed. Section 3 presents the variable temperature data taken and confirms the reliability of our equipment by describing the experimental consistency tests made during commissioning. Section 4 provides theoretical calculations for the three metals studied. In Section 5 we discuss all the results presented, compare our data with that in the literature and summarise our conclusions.

2. Design of low-intensity luminescence equipment

Commercial equipment for measuring the luminescence of semiconductors where the intensity of emission is typically 10^5 times higher than in metals often use coloured glass filters, monochromators and predispersers [9,10]. However, monochro-mators and predispersers can reduce the emission intensity for a metal to below the sensitivity of the detector. Of even greater concern, the luminescence emission intensity of coloured glass filters and lenses is usually greater than that from metals. Other

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problems with commercial equipment include luminescence from anodised sample holders and sample mounting techniques/adhesives.

Fig. 1 shows a schematic diagram of our new instrument. Samples were excited using a Coherent Argon Ion Laser lasing at 488 nm. Laser power was monitored using a germanium photodiode detector. The samples were mounted on an x–y–z-translatable copper sample holder. The position of the sample holder can be adjusted to compensate for thermal contraction inside the Cryomech ST405 cryostat with optical windows. An Olympus Optics UPLSAPO $4 \times$ microscope objective was used to collect the luminescence emission. A Semrock Raman RazorEdge® dichroic filter was positioned after the objective to reject any elastically scattered excitation laser light. The photoluminescence emission was then focussed onto a Bentham TM300 mono-chromating spectrometer and the spectrum collected using an EG&G PARC Model 1453A silicon photodiode array detector. Luminescence from optical components was minimised by using high-purity fused silica lenses and a Spectrosil 2000 window in the cryostat. A reflecting rather than an absorbing filter was used to remove elastically scattered laser light. Mounting the samples on to a silicon wafer eliminated significant luminescence from the sample holder within the range of wavelengths measured. All adhesives were carefully located behind the sample and could not be illuminated by the laser. Post-sample optics were enclosed to prevent any background light from entering the spectrometer.

3. Results and consistency tests

3.1. Room temperature measurements

The samples investigated were 99.999% (5 N) purity Au foil and 99.99% (4 N) purity Au wire, 99.9999% (6 N) and 99.95% (3 N) purity Cu, and 99.8% (2 N) purity Nb. The metals were polished and then cleaned in acetone and isopropanol. Room temperature photoluminescence emission spectra for 5 N and 4 N Au are presented in Fig. 2 in which the peak in the emission of the 5 N Au is located at 525 nm and the full-width at half-maximum (FWHM) is 90 nm. Also shown is a theoretical curve discussed in the next section. The normalised spatially resolved 5 N Au spectra shown in Fig. 3 show that the peak intensity of the spectra can vary by more than an order of magnitude without the shape of the spectrum changing significantly. Similar spatially resolved data on 4 N Au (not shown) give some spectra that we associate with local
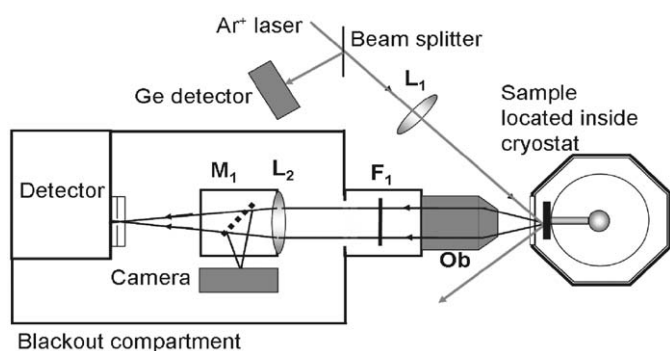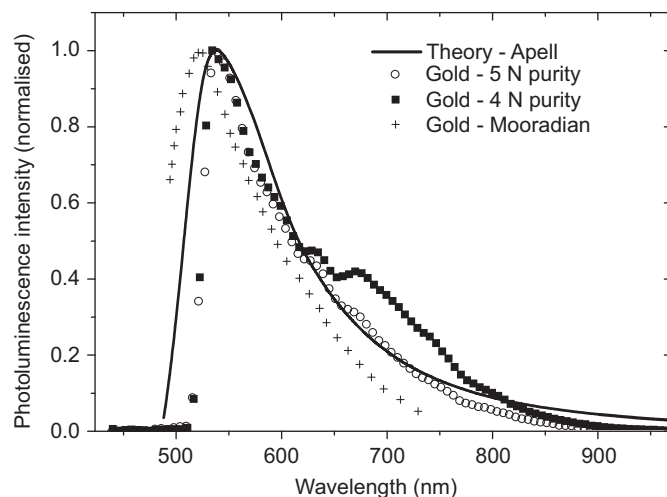

Fig. 2. Comparison of the normalised photoluminescence emission spectrum intensity for gold at 295 K with the theory [8]. Data from this work for 5 N purity and 4 N purity gold and data from Mooradian [6] are displayed. The theoretical curve [8] includes experimental data for optical constants taken from the CRC handbook [11] and the density of states calculated using CASTEP.
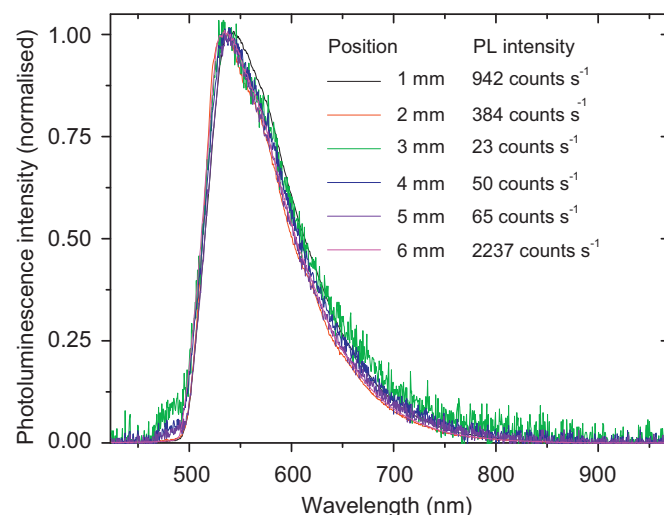

Fig. 3. Normalised photoluminescence emission spectra of 5 N gold measured at different positions across the sample surface. Measurements were made across the sample at 1 mm intervals. The legend gives the number of counts per second at the peak of the intensity at each of six positions. The edges of the sample were located at 0 and 6 mm.

regions of high-purity 5 N gold as well as spectra that are consistent with the presence of impurities and give an additional peak at ∼700 nm (as seen in Fig. 2). Fig. 4 shows data taken over a period of the week after polishing during which the Au was stored in air. Neither the shape nor the intensity of the Au spectrum changed significantly.

Additional experiments during commissioning provide confidence in the data. The luminescence of the post-sample optical components was measured by rotating the sample and reflecting the laser directly through the objective. The major peak observed after rotation occurs at ∼800 nm, which disappears when the sample is correctly positioned as shown in Fig. 1. The objective is positioned so that no light reflected from the cryostat window passes into the objective—this is confirmed by showing that the data at room temperature are unchanged when the window is removed. Reproducibility of optical alignment currently causes an uncertainty in emission intensity of ∼20%.

Fig. 1. Schematic diagram of photoluminescence equipment. The laser excitation beam and luminescence emission are focussed using the lenses L_1 and L_2, respectively. Luminescence emission from the sample is collected using the microscope objective Ob, and conditioned using the dichroic filter F_1. The mirror M_1 is used to direct light onto the camera for use in variable temperature alignment.
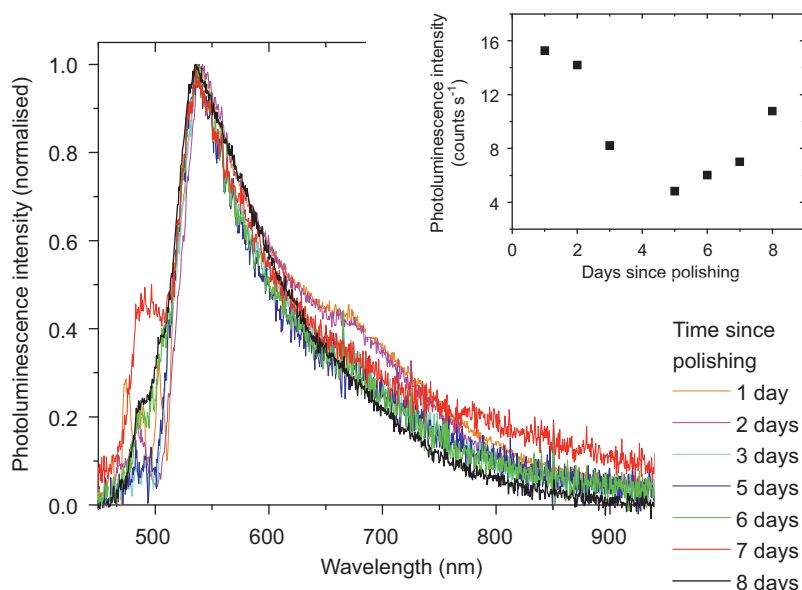
Fig. 4. Normalised photoluminescence spectra of 5 N gold collected over a period of one week. Spectra were measured at 300 K with zero time set as the end of the sample polishing process. The inset graph shows the maximum luminescence intensity as a function of time. Typical photoluminescence excitation intensities were 60 mW.
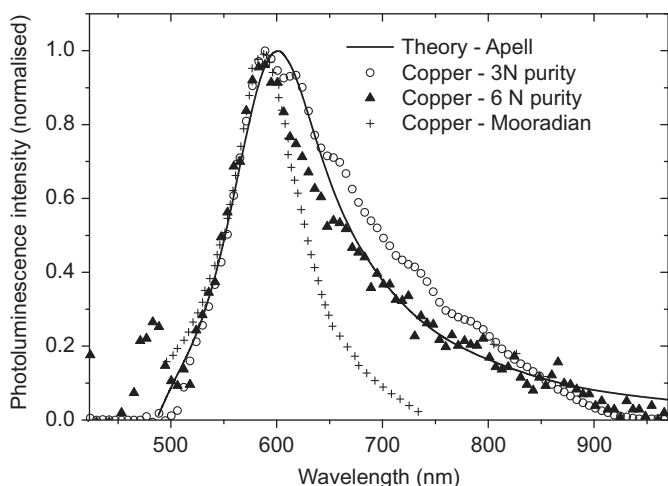

Fig. 5. Comparison of measured normalised photoluminescence emission spectra at 295 K for copper with theory. Also shown is experimental data from Mooradian [6]. The theoretical curve [8] includes experimental data for optical constants taken from the CRC handbook [11] and the density of states calculated using CASTEP [12].

Fig. 5 shows the room temperature photoluminescence emission spectra for Cu that has a peak emission wavelength at 588 nm and an FWHM value of 145 nm. Fig. 5 shows a comparison between our experimental data for Cu and those from Mooradian [6]. There is very good qualitative agreement between the different datasets for the peak emission wavelength although the peak widths are somewhat larger in our data. The higher purity 6 N copper shows a narrower spectrum that is more like the Mooradian results than the 3 N copper. Given the broad agreement between these spectra, Fig. 6 shows very interesting aging data equivalent to that shown for Au in Fig. 4. Unlike Au, there is a clear increase in the intensity of the spectra for Cu when exposed to air for long periods. Furthermore although the intensity broadly increases, the shape of the spectra does not change markedly.

Fig. 7 shows the data for unpolished Nb when the dichroic Raman RazorEdge® filter is both in the standard position and after it has been rotated by 4°. We conclude that the rotation only affects the cut-off wavelength that is usually 535 nm and not the shape of the spectrum at higher wavelengths for all the data presented in this work. After the niobium sample had been polished, we found that the signal was below the noise floor of our instrument and remained so thereafter (for more than one week).

Fig. 8 shows the peak emission intensity is linear with excitation power for the Au, Cu and unpolished Nb samples. Sample spectra do not change after exposure to a laser power of up to 120 mW. We conclude the linear power dependence is characteristic of these materials and that no damage has occurred to the samples throughout these experiments.

3.2. Variable temperature measurements

Variable temperature measurements, similar to those shown in Figs. 2, 5 and 7 were made between 300 and 100 K for all three metals. A translation stage was used to correct for movement of the sample to within 100 μm, caused by thermal contraction, by using the removable mirror and camera shown in Fig. 1. Spectra obtained were independent of the thermal history for the measurement. Analysis of the peak intensity and peak width of the spectra as a function of temperature are shown in Figs. 9 and 10. Au and Cu show a small reproducible increase in peak intensity of ~20% and decrease in the peak width by ~10% when the temperature is decreased from 300 to 100 K. No changes were observed for the peak intensity or the peak width over the same temperature range to within ±20% for the unpolished Nb.

4. Theoretical calculations

Theoretical work on luminescence emission from noble metals has been carried out by Apell et al. [8]. The intensity of the luminescence emission spectrum (I_{lum}) can be considered to be due to an interplay between the density of states ($g(E)$) and the optical properties—the real part of the refractive index, n, the extinction coefficient, κ, and the absorption coefficient, $\alpha(\omega)$. The
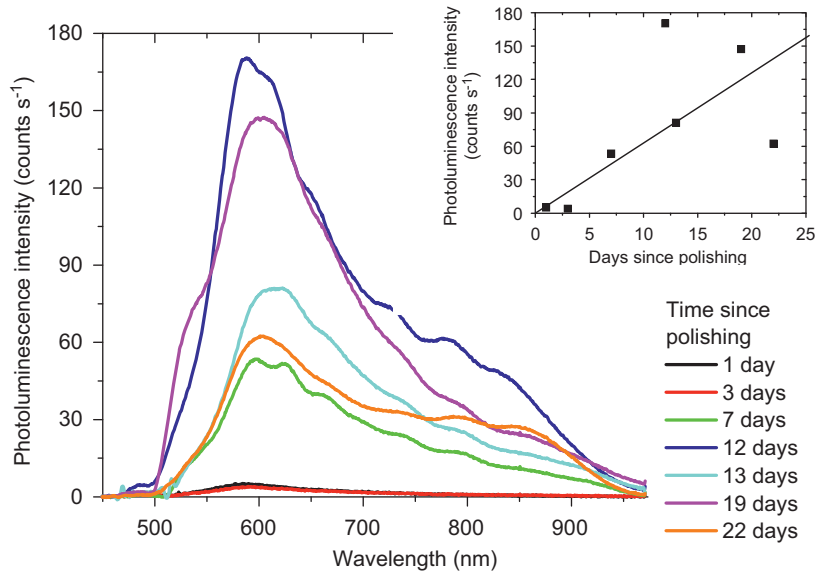
Fig. 6. Photoluminescence spectra for 6 N copper collected over a 22 day period. Spectra were measured at 300 K with zero time set as the end of the sample polishing process. The inset graph shows the maximum luminescence intensity as a function of time. Typical photoluminescence excitation intensities were 60 mW.
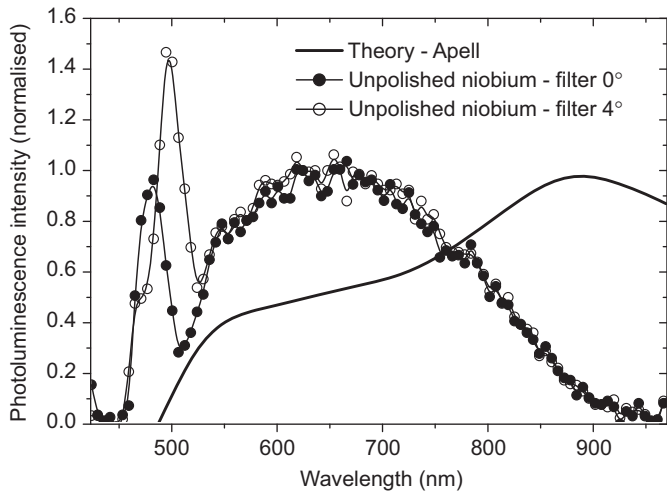

Fig. 7. Comparison of the photoluminescence emission spectrum of 2 N unpolished niobium measured at 295 K with theory [8]. Rotation of the dichroic filter by 4° only changes the transmission cut-off wavelength but not the shape of the spectrum. The theoretical curve [8] for Nb includes experimental data for optical constants taken from the CRC handbook [11] and the density of states calculated using CASTEP [12].
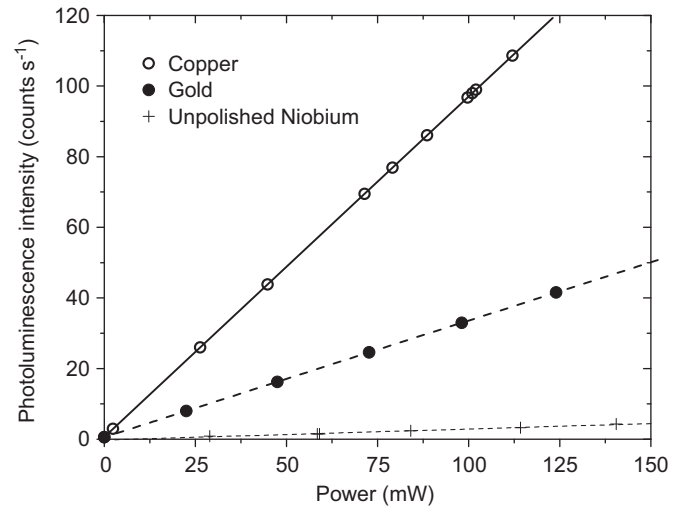

Fig. 8. Photoluminescence peak intensity versus excitation power for copper, gold and unpolished niobium.

Fig. 9. Photoluminescence peak intensity versus temperature for gold, copper and unpolished niobium. These data have been normalised to unity at 100 K.

luminescence emission includes the excitation and emission frequencies, ω_1 and ω_2, and is given by

$$I_{\text{lum}} \approx \frac{\omega_2}{\alpha(\omega_2) + \alpha(\omega_1)} \cdot \frac{4}{(1 + n_2)^2 + \kappa_2^2} \cdot \frac{1}{(n_2^2 + \kappa_2^2)} \cdot \int_{E_f - \omega_1}^{E_f - \omega_2} [g(E)]^2 \, dE.$$

(1)

The theoretical emission spectra for Au, Cu and Nb were calculated and are presented in Figs. 2, 5 and 7. Experimental values for n, κ, α were obtained from reflection and transmission measurements [11] and $g(E)$ from calculations using CASTEP [12]. Theory attributes the factor ~50 lower peak in the intensity of the emission from Nb compared to Au and Cu to the real part of the refractive index being a factor ~5 higher and the density of states ~2 eV below the Fermi energy being a factor of ~4 lower than Au and Cu. In Apell's original work [8] and in Fig. 2, there is broad agreement between theory and experiment for the shape of the
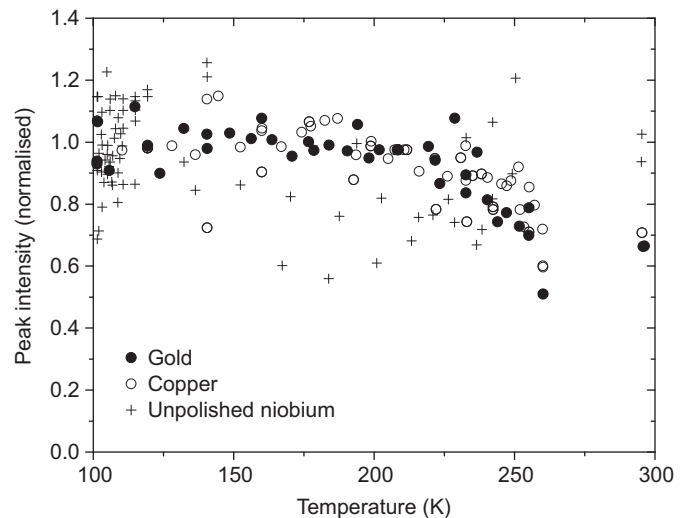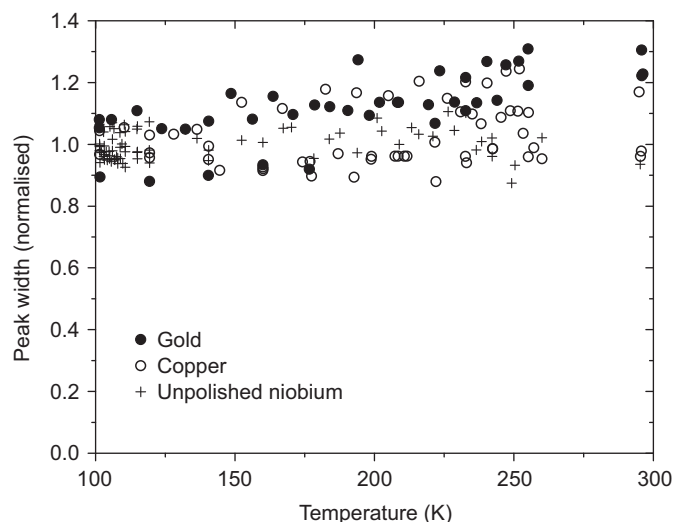
Fig. 10. Full-width at half-maximum of the photoluminescence spectrum versus temperature for gold, copper and unpolished niobium. These data have been normalised to unity at 100 K.

spectrum for Au. Fig. 5 shows there is good agreement between the data for Cu and theory. There are very significant discrepancies between the shape of the spectrum obtained from theory for Nb and experiment for unpolished Nb as shown in Fig. 7.

5. Discussion and conclusions

We have designed, built and tested an instrument for measuring low intensity luminescence spectra as a function of temperature. We have measured the luminescence spectra of Au, Cu and unpolished Nb between 100 K and room temperature that are at most, weakly temperature dependent.

Our data for high-purity 5 N Au agree closely with experimental data and theoretical predictions from the literature. Consistent with the noble properties of gold, we find (Fig. 2) the spectra are unaffected by exposure to air [13] and conclude that the temperature dependence of the data is accurate to about $\pm 20\%$. The interpretation of the copper luminescence data is less clear cut. Our room temperature spectrum has a similar shape to those found for Cu samples prepared and maintained at 10^{-9} Torr [7] as well as Mooradian's data (as shown in Fig. 5). Furthermore, the intensity of the Cu spectrum at room temperature after polishing is similar to that for Au as required by theory and the shape of the spectrum is consistent with theory. Such consistency points to accurate measurements of Cu. However the data shown in Fig. 6 undermines associating the spectrum with pure copper

since the intensity of the spectrum increases with exposure to air but does not radically change shape. The well-known effects of roughness of metals that can increase the luminescent signal by local-field enhancement in protrusions provide no explanation because even were surface reconstruction to occur it would reduce, not increase the signal. We cannot yet rule out problems associated with adsorbates and/or oxides on rough samples providing strong sources of luminescence [7,14] or safely interpret the data in Fig. 6 by assuming that the adsorbates and/or oxides associated with copper produce a similar spectrum to pure copper itself. Taking the theoretical calculations for Nb at face value and the lack of signal measured for newly polished Nb, we conclude that the signals we have found for unpolished Nb should be associated with contaminants and that the signal from pure Nb still remains below the sensitivity of our instrument.

It is clear that making accurate variable temperature measurements on metals other than Au, and on superconductors in particular, remains a formidable challenge. Recently, we have measured room temperature luminescence spectrum for $YBa_2Cu_3O_{7-\delta}$ that was found to have peak emission intensity between that of Nb and Cu. Future work will include further improvements in sensitivity of our photoluminescence emission spectra measurements and extending them to include magnetic fields. We expect the investigations using photoluminescence will provide an insight into the electronic processes occurring in the normal and superconducting state of a range of metals.

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