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# Optical Reflectivity of Liquid Metals at their Melting Temperatures

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We utilize the concept of electron-phonon dominated optical conductivity and the Drude theory of optical properties of metals, as applied by Ujihara,<sup>1</sup> and the theory of melting in simple metals of Omini,<sup>2</sup> based on the Percus-Yevick<sup>3</sup> collective coordinate (liquid phonon) theory of simple liquids, to calculate the optical reflectivity in a variety of liquid metals. We compare the reflectivity of the metals treated by Ujihara, and extended by Siegel<sup>4</sup> (Ag, Au, Al, Cu, Fe, Ni, Co) at their melting temperatures in the solid and liquid phases to determine if the change in phonon spectrum and electron-phonon collision frequency in the solid to the Percus-Yevick "liquid phonon spectrum" and electron-liquid phonon collision frequency in the liquid affects the optical properties. Later we extend the calculations of reflectivity in the liquid metals beyond their melting temperatures. This is a valid criterion of whether the Percus-Yevick liquid phonon approach to electron-disorder scattering in liquid metals is applicable in evaluating the high frequency, optical properties of liquid metals, since we can readily determine if the calculated melting entropy of Ujihara corresponds to an expected change in the optical conductivity, dielectric constant and reflectivity.

## 1 DRUDE THEORY AND ELECTRON-PHONON COLLISIONS IN SOLID METALS

Ujihara<sup>1</sup> has recently calculated the high temperature reflectivity of Al, Cu, Ag and Au (among others) up to their melting temperatures at three

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wavelengths (0.69, 1.06 and 10.6 microns). We follow Ujihara's development of the Drude theory and electron-phonon collision concepts in the calculation of the optical conductivity, dielectric constant and temperature dependent reflectivity and skin depth since we shall rely on these techniques rather heavily in our treatment of liquid metals.

Within the Drude theory for a solid metal, the dielectric constant is given by

$$\epsilon^s(T) = \epsilon_1^s(T) + \epsilon_2^s(T) = 1 - [\omega_p^{s2}(T)/\omega^2 + \omega_c^{s2}(T)] - \frac{i \omega_p^{s2}(T) \omega_c^s(T)}{(\omega^2 + \omega_c^{s2}(T)) \omega} \quad (1)$$

where  $\epsilon_1$  and  $\epsilon_2$  are respectively the real and imaginary part of the complex dielectric constant,  $\omega$  is the incident optical frequency,  $\omega_c^s$  is the average electron-phonon collision frequency and  $\omega_p^s$  is the electron plasma frequency in the metallic solid.

$$\omega_p^s(T) = 4\pi n^s(T) e^2/m_e^* \quad (2)$$

where  $n^s(T)$  is the temperature dependent electron density in the solid metal,  $e$  is the electron charge and  $m_e^*$  is the electron effective mass. The Drude result is derivable from the Boltzmann equation assuming an average relaxation time,  $\tau_c^s = \omega_c^{s-1}$  for the electron distribution via the electron-phonon collisions. The real and imaginary parts of the complex dielectric constant are

$$\epsilon_1^s(T) = 1 - [\omega_p^{s2}(T)/\omega^2 + \omega_c^{s2}(T)] \quad (3)$$

$$\epsilon_2^s(T) = -\omega_p^{s2}(T) \omega_c^s(T)/(\omega^2 + \omega_c^{s2}(T)) \omega \quad (4)$$

and are temperature dependent because  $\omega_p^s$  and  $\omega_c^s$  are. In terms of the complex refractive index,  $\epsilon^{1/2}$ , the optical reflectivity in the Drude theory is

$$R^s(T) = |\epsilon^{s1/2} - 1/\epsilon^{s1/2} + 1|^2 \quad (5)$$

At 300° K.,  $\omega_p^s \sim 10^{16} \text{ sec}^{-1}$  and  $\omega_c^s \sim 10^{14} \text{ sec}^{-1}$  in solid metals. In Table 1 we list  $\omega_p^s$  and  $\omega_c^s$  values for a variety of solid metals (later to be compared with these values in the liquid state).  $R$  is about unity at the three wavelengths considered here, since for  $\lambda = 0.69$  microns,  $\omega_p^{s2} > \omega^2 > \omega_c^{s2}$  and for  $\lambda = 10.6$  microns,  $\omega \sim 10^{14} \text{ sec}^{-1}$ , so  $\epsilon^{s1/2}$  is large in both cases.

Following Ujihara we make the approximation that the  $\omega_p^s(T)$  temperature dependence is small because  $n^s(T)$  is small, and concentrate on  $\omega_c^s(T)$ , assuming the high temperatures do not create any new band structure effects. In the Debye phonon spectrum model of the actual phonon spectrum in the solid metal

$$\omega_c^s(k, T) = K^s |k| T^5 \int_0^{\theta_D^s/T} (z^4 dz/e^z - 1) \quad (6)$$

where we have assumed the scattering mechanism to be normal processes on a spherical Fermi surface, and where  $\theta_D^s$  is the Debye temperature,  $T$  is the temperature and  $K$  is a constant including the total scattering cross section of the isolated metal atom, the ion mass, the Debye wavenumber and other constants. We further assume that  $\theta_D^s$  is not temperature dependent. Then  $K$  is independent of temperature. Also

$$\omega_c^s(T) = \int_{FS} \omega_c^s(k, T) dk \quad (7)$$

but since  $k_B T < E_F$ , the Fermi energy, we can utilize an iso-thermal electron distribution for  $T < T_M$ , the melting temperature (and also in the liquid state for  $T \geq T_M$ , as we shall see later on). We can then rewrite (6) as

$$\omega_c^s(T) = K^s T^5 \int_0^{\theta_D^s/T} (z^4 dz/e^z - 1) \quad (8)$$

where  $K^s$  contains  $K$  and the mean value of  $|k|$ . Ujihara, in an appendix, shows how  $\omega_c^s$  is an increasing function of  $T$ , since

$$d\omega_c^s(T)/dx = K^s \theta_D^{s5}/x^6 \left[ \int_0^x (5 z^4 dz/e^x - 1) - \int_0^x (5 z^4 dz/e^z - 1) \right] < 0 \quad (9)$$

for  $0 < z < x$ , our region of integration in (8), where  $x = \theta_D^s/T$ , so that  $d\omega_c^s(T) > 0$ .

Ujihara then predicts that  $\epsilon_1^s < 0$  at the frequencies of interest,  $|\epsilon_1^s|$  (300°K.) is large and  $\epsilon_1^s$  is an increasing function of  $\omega_c^s$ , and thus of  $T$ . Also,  $\epsilon_2 < 0$  and  $\lim_{T \rightarrow 0, \infty} \epsilon_2^s = 0$  and  $\epsilon_2^s$  is a minimum when  $\omega = \omega_c^s$ . Also, since the skin depth is defined as

$$\delta^s(T) = c/\omega k^s(T) \quad (10)$$

where  $c$  is the speed of light in vacuum and  $k$  is shown to decrease with increasing  $T$ ,  $\delta^s(T)$  increases as  $T$  increases. Lastly, he finds that

$$dR/d\omega_c^s = [(\omega_p^s/\omega)^2 (|\epsilon| + 1)/2^{1/2} |\epsilon| [|\epsilon| + 1 + 2^{1/2} (|\epsilon| + \epsilon_1)^{1/2}]^2 (|\epsilon| + \epsilon_1)^{1/2} d\epsilon_1^s/d\omega_c^s] \quad (11)$$

and

$$d\epsilon_1^s/d\omega_c^s = 2\omega_p^{s2} \omega_c^s/(\omega^2 + \omega_c^{s2})^2 > 0 \quad (12)$$

so that  $dR/d\omega_c^s < 0$ , and as  $\omega_c^s$  rises when  $T$  does,  $R$  drops. The calculated  $\delta(T)$  and  $R(T)$  curves are shown in Figures 7-12 of Ujihara's paper, at 0.69 microns ( $\omega = 2.72 \times 10^{15} \text{ sec}^{-1}$ ), 1.06 microns ( $\omega = 1.78 \times 10^{15} \text{ sec}^{-1}$ ) and 10.6 microns ( $\omega = 1.78 \times 10^{14} \text{ sec}^{-1}$ ).

## 2 PERCUS-YEVICK THEORY OF LIQUIDS VIA LIQUID PHONONS

Ominiz has recently applied the Percus-Yevick<sup>3</sup> collective coordinate theory of liquids to calculate the melting entropy of simple metals. This theory replaces the potential energy in the total liquid Hamiltonian

$$1/2 \sum_{i \neq j} (2\pi)^{-3} \int d^3k e^{ik \cdot (x_i - x_j)} \tilde{V}(k) = 1/2 \sum_{i \neq j} V(x_i - x_j) \quad (13)$$

by

$$V^{PY} = 1/2 \sum_{i \neq j} \sum_{\{k\}} v_k e^{ik \cdot (x_i - x_j)} \quad (14)$$

where the coefficients  $v_k$  are determined to optimize the calculation. Defining  $3N$  collective coordinates (liquid phonons)

$$q_k = \sum_i e^{ik \cdot x_i} \quad (15)$$

the potential energy becomes that of an assembly of  $3N$  harmonic oscillators

$$V^{PY} = 1/2 \sum_{\{k\}} v_k (q_k q_{-k} - N) \quad (16)$$

with frequencies

$$\omega_k^2 = k^2 k_B T / m (1 + v_k / k_B T) \quad (17)$$

Utilizing the Ascarelli-Harrison-Paskin<sup>5</sup> relation between the long wavelength limit of the liquid structure factor,  $S(0)$  and the set  $v_k$

$$S(0) = k_B T / (k_B T + v_k) \quad (18)$$

(17) may be rewritten as

$$\omega_k^2(T) = k^2 k_B T / m S(0) \quad (19)$$

where  $m$  is the atomic mass. This dispersion relation for the liquid phonon frequency spectrum has, as does the Debye phonon spectrum in the solid phase, a high frequency cut-off at

$$(\omega^{PY}(T))_{MAX}^2 = (18\pi^2 \rho(T)/m)^{2/3} k_B T / m S(0) \quad (20)$$

associated with a maximum wavevector, analogous to  $k_{Debye}$  of

$$Q(T) = (18\pi^2 \rho/m)^{1/3} = 3^{1/3} k_{Debye} \quad (21)$$

This is derived from the condition that

$$(L/2\pi)^3 (4\pi Q^3/3) = 3N \quad (22)$$

defining a radius in  $k$  space of magnitude  $Q$  which contains the  $3N$   $k$  values

permitted in the Percus-Yevick collective coordinate model of a liquid.

### 3 OPTICAL PROPERTIES OF LIQUID METALS

We have now a Debye-like liquid phonon model of the atomic vibrations in a simple liquid metal, involving structural disorder through the S(O) in the previous expressions. Having this, we should be able to repeat the analysis of Section 1 to arrive at  $R^L(T)$  and  $\delta^L(T)$ , even at  $T_M$ , so that we can see the effect of Omini's predicted change in system entropy upon melting on the optical reflectivity and skin depth through the melting temperature.

We rewrite the Drude dielectric constant for a liquid metal identically to that in a solid metal, as

$$\epsilon^L(T) = \epsilon_1^L(T) + i\epsilon_2^L(T) = 1 - \left[ \frac{\omega_p^{L2}(T)}{\omega^2 + \omega_c^{L2}(T)} \right] - i\omega_p^{L2}(T)\omega_c^L(T)/(\omega^2 + \omega_c^{L2}(T))\omega \quad (23)$$

with real and imaginary parts

$$\epsilon_1^L(T) = 1 - \omega_p^{L2}(T)/(\omega^2 + \omega_c^{L2}(T)) \quad (24)$$

$$\epsilon_2^L(T) = -\omega_p^{L2}(T)\omega_c^L(T)/(\omega^2 + \omega_c^{L2}(T))\omega \quad (25)$$

The difference from the Drude dielectric constant for the solid metals is the appearance of  $\omega_p^L$  and  $\omega_c^L$  in place of  $\omega_p^s$  and  $\omega_c^s$ . It remains to determine how different the plasma frequency and electron-phonon collision frequency are in the liquid state. This approach is perhaps not as fundamental as a complete reformulation of the concept of a collision frequency in terms of the disorder scattering of electrons in liquid metals, but is an interesting application of the Percus-Yevick concept of liquid phonons to treating a metallic liquid in a form identical to that for a metallic solid and a useful initial model for simplified calculation of approximate optical properties.

The electron plasma frequency in the liquid metal is

$$\omega_p^L(T) = 4\pi n^L(T)e^2/m_c^{**} \quad (26)$$

where the free electron density has changed from its value in the solid metal, and the electron effective mass has changed since the periodic potential of the solid metal has been destroyed upon melting. The liquid metal has a reflectivity

$$R^L(T) = |(\epsilon^{L1/2}(T) - 1)/(\epsilon^{L1/2}(T) + 1)|^2 \quad (27)$$

and the liquid metal skin depth is

$$\delta^L(T) = c/\omega k^L(T) \quad (28)$$

Our problem now reduces to an investigation of the mechanisms and

physical content of  $\omega_p^L(T)$  and  $\omega_c^L(T)$ , as Ujihara did for solid metals. Once these are obtained, the temperature dependent liquid metal reflectivity and skin depth can be easily evaluated in this first, simple approximation to the actual electron-disorder scattering in the liquid metal optical conductivity. The electron-liquid phonon collision frequency in the liquid metal,  $\omega_c^L(T)$ , is easily found using the Percus-Yevick collective coordinate theory of simple liquids, in which the actual electron-disorder scattering contribution to the optical conductivity of the liquid metal is replaced by an effective electron-liquid phonon scattering frequency, which then determines the optical conductivity in the same way Ujihara utilized this approach in solid metals using the electron-phonon collision frequency. Treating the Percus-Yevick liquid phonon spectrum like the Debye phonon spectrum in a solid metal, what we need to evaluate is the change in electron distribution due to collisions with the liquid phonons, whose distribution is temperature dependent, as in a solid metal. We define a Percus-Yevick temperature for the liquid phonon spectrum,  $\theta_{PY}$  by

$$\hbar\omega^{PY}(T) = k_B \theta_{PY}(T) \quad (29)$$

analogous to the definition of the Debye temperature in a solid metal

$$\hbar\omega_D(T) = k_B \theta_D(T) \quad (30)$$

We shall assume that, as in the solid metal case

$$\omega_c^L(T) = K^L T^5 \int_0^{\theta_{PY}/T} z^4 dz / (e^z - 1) \quad (31)$$

in analogy with (6), where  $K^L$  is a constant like  $K^S$  in (6). The use of this relation to represent the collision frequency in a liquid is the major weak point of our theory, but is justified in the believable answers we shall obtain. We shall see that the success of this approach follows because in the liquid, as in the solid, we have replaced the N body collision problem by a 3N collective boson-electron collision problem, and once this is done, the detailed nuances that separate the definition of the solid metal from the liquid metal are all removed except in so far as they influence the values for  $\theta_D$  and  $\theta_{PY}$ . All we have done is to replace the Debye temperature characterizing the phonon spectrum in the solid with the Percus-Yevick temperature, characterizing the liquid phonon spectrum in the liquid. The liquid phonons, like the solid state phonons, are considered as a boson gas whose distribution is temperature dependent and whose effect is to replace the detailed structure of the liquid metal by a simple quasiparticle spectrum, which scatters electrons producing a finite  $\tau_c^L(T) \sim \omega_c^L(T)^{-1}$ , which can be used to calculate an approximate liquid metal optical conductivity, and thus the dielectric constant, reflectivity and skin depth. The temperature dependence in all of

these expressions has its origin in the temperature dependence of  $\theta_{PY}$ . For the skin depth, the temperature dependence is analogous to that in the solid metal, in that, using

$$dk/d\omega_c^L = (\omega_c^L/2k)(\omega_p^{L2}/(\omega^2 + \omega_c^{L2})^2 [((2 - \omega_p^{L2}/\omega^2)/2(1 - \omega_p^{L2}(2 - \omega_p^{L2}/\omega^2) (\omega^2 + \omega_c^{L2})^{-1})^{1/2}) - 1] \quad (32)$$

to show that  $k$  is an increasing function of  $\omega_c^L$ , which is in turn an increasing function of  $T$ , so that  $\delta^L(T)$  is an increasing function of  $T$ , as Ujihara argued for solid metals.

The plasma frequency,  $\omega_p^L(T)$  must also be evaluated in the liquid metal. As Ujihara has done, we assume  $\omega_p^L$  independent of  $T$  relative to the strong dependence of the collision frequency,  $\omega_c^L$  on  $T$  we expect to find. In a random medium such as a liquid metal, it is not clear that  $m_e^{**}$  has a well defined meaning, but for simplicity we argue that  $m_e^{**}(T_M) = m_e^*(T_M)$  i.e. a melting metal at  $T_M$  is nearly as disordered as the liquid phase it is in equilibrium with, and the liquid for any greater temperature, so that  $m_e^*$  can be used for liquid metals as well as for solid metals. In solid metals

$$m_e^{*-1} = \hbar^{-2} d^2 E^s / dk^2 \quad (33)$$

so that in liquid metals

$$m_e^{** -1} = \hbar^{-2} d^2 E^L / dk^2 \quad (34)$$

What is needed is the electron dispersion relation in the liquid metal,  $E^L(k)$ . In its absence we are forced to take  $m_e^{**} = m_e^*$ , so that  $\omega_p^S = \omega_p^L$ . This is further supported by the fact that, since  $\omega_p^S(T)$  is such a weak function of  $T$  in the solid metal, it should be similarly weak in the liquid metal, since even there  $k_B T_M \ll E_F$ , so that the high temperatures do not perturb the electron distribution function much.

In summary, we calculate  $\epsilon_1^L(T)$  and  $\epsilon_2^L(T)$  from (24) and (25), using  $\omega_p^L \sim \omega_p^S$  independent of  $T$ , and (31) for  $\omega_c^L$

$$\epsilon_1^L(T) = 1 - \omega_p^{S2}/(\omega^2 + \omega_c^{L2}(T)) \quad (35)$$

$$\epsilon_2^L(T) = -\omega_p^{S2} \omega_c^L(T)/(\omega^2 + \omega_c^{L2}(T)) \omega \quad (36)$$

To proceed we must evaluate  $\omega_c^L(T)$  from (31).

#### 4 EVALUATION OF THE LIQUID METAL COLLISION FREQUENCY

We must evaluate

$$\omega_c^L(T) = K^L T^5 \int_0^{\theta_{PY}/T} z^4 dz / (e^z - 1)$$



where

$$\theta_{PY}(T) = (\hbar/k_B) \omega_{MAX}^{PY}(T) = (k_B T/mS(O))^{1/2} (18\pi^2 \rho(T)/m)^{2/3} k_B/\hbar \quad (37)$$

In Table I we list the  $S(O)$  values for a variety of liquid metals at  $T_M$ , and the  $Q$  values, both calculated independently and transcribed from Omini's paper. Since  $Q = 3^{1/3} k_D$ ,  $\omega_{MAX}^{PY} = Q(k_B T/mS(O))^{1/2} = 3^{1/3} k_D (k_B T/mS(O))^{1/2}$  and

$$\hbar \omega_D = k_B \theta_D = \hbar v_s k_D = \hbar v_s (6\pi^2 N)^{1/3}/L \quad (38)$$

where  $v_s$  is the sound speed in the solid metal,

$$k_D = k_B \theta_D/\hbar v_s \quad (39)$$

and the Percus-Yevick temperature can be expressed as

$$\begin{aligned} \theta_{PY}(T) &= 3^{1/3} (k_B^2 \theta_D(T)/\hbar^2 v_s(T)) \\ (k_B T/m S(O))^{1/2} &= \hbar/k_B (\omega^{PY})_{MAX}/k_B \end{aligned} \quad (40)$$

Thus, we can use the above expression for  $\theta_{PY}$  in terms of  $\theta_D(T)$ ,  $v_s(T)$  and  $S(O)$  or the expression in terms of  $\rho(T)$  and  $S(O)$  to evaluate the upper limit of the integral (31). We must note that there is a discrepancy between our  $Q$  values and Omini's, for example for liquid Li to Sn in Table I. It is not clear how Omini arrives at his, so we calculated the ones used here from Goldschmidt atomic radii<sup>7</sup> via

$$Q = (18\pi^2 \rho/m)^{1/3} = (18\pi^2/v)^{1/3} = (18\pi^2/(4/3)\pi(d/2)^3)^{1/3} \quad (41)$$

where  $d = 2r$  is the atomic diameter.

We might also note that the plasma frequency values

$$\omega_p^L = \omega_p^S = (4\pi n e^2/m_e^*)^{1/2} \quad (42)$$

where, in terms of the Goldschmidt radii

$$n = \tilde{n}/V = \tilde{n}/(4/3)\pi(d/2)^3 \quad (43)$$

where  $\tilde{n}$  is the effective number of valence electrons per atom, and its exact value for any metal is open to question. For the case of Na, K, Al, Cu, Au and Ag the  $\omega_p^S$  values are nearly equal to those quoted by Pines<sup>6</sup> and Ujihara. Thus, the  $\theta_{PY}$  values we use are open to some question, and are compared in Table I with those of Omini for Li-Sn. The uncertainties in  $\tilde{n}$  are just as important to our calculation as those in  $V$ , via the Goldschmidt radii, and in  $\omega_p^L$ .

Also shown in Table I are the  $\omega_c^L(T_M)$ , and those  $\omega_c^L$  values at  $1.5 T_M$  and  $2 T_M$  calculated both for our  $Q$  values and Omini's for Li-Sn. For the cases Na, K, Ag, Au, Cu and Al, treated by Ujihara in the solid state, we compare our calculated  $\omega_c^L(T_M)$  values. We see that they fall in the same range, but are

TABLE I  
 Input parameters used in optical properties calculation, including a comparison of the Omini<sup>2</sup> Q and  $\theta_{PY}$  values with those calculated from Goldschmidt radii.

Liquid Metal	S(0) <sup>(2)</sup>	Q <sup>(2)</sup>	Goldschmidt			T <sub>M</sub> (°K)	T <sub>M</sub> θ <sub>PY</sub> (°K)	V <sub>atom</sub> × 10 <sup>-24</sup> (cm <sup>3</sup> )	r <sub>Goldschmidt</sub>	ñ <sup>8</sup>	ω <sub>p</sub> <sup>L,S</sup> × 10 <sup>15</sup> (sec <sup>-1</sup> )	(2)T <sub>M</sub> θ <sub>PY</sub> (°K)
			Q × 10 <sup>8</sup> (cm <sup>-1</sup> )	Q <sup>(2)</sup>	T <sub>M</sub> (°K)							
Li	0.025	1.975	2.219	452	625	16.21	1.57	1	14.00	556		
Na	0.025	1.625	1.815	371	254	29.65	1.92	1	10.40	227		
K	0.025	1.307	1.465	337	150	56.47	2.38	1	7.51	134		
Rb	0.025	1.223	1.383	312	92	67.03	2.52	1	6.89	72		
Cs	0.025	1.138	1.291	301	68	82.45	2.70	1	6.21	77		
Mg	0.025	1.901	2.178	924	468	17.16	1.60	2	19.30	409		
Al	0.025	2.108	2.436	933	500	12.25	1.43	3	27.90	432		
Zn	0.025	2.240	2.543	693	289	10.77	1.37	2	24.30	254		
Ga	0.025	2.102	2.580	303	188	10.31	1.35	3	30.40	153		
Pb	0.009	1.754	1.653	600	163	39.29	1.75	4	18.00	173		
Tl	0.008	1.805	2.050	576	212	20.58	1.70	3	21.50	187		
Sn	0.008	1.845	2.206	505	281	16.52	1.58	4	27.60	235		
Cd	0.025	—	2.292	594	184	14.71	1.52	2	20.80	—		
Cu	0.025	—	2.722	1357	439	8.78	1.28	0.84	17.40	—		
Au	0.008	—	2.419	1336	388	12.51	1.44	1.14	17.00	—		
Ag	0.008	—	2.419	1234	389	12.51	1.44	1.14	17.00	—		
Fe	0.025	—	2.765	1809	549	8.38	1.26	0.84	17.90	—		
Co	0.025	—	3.003	1768	574	6.54	1.16	0.84	20.20	—		
Ni	0.025	—	2.787	1725	527	8.18	1.25	0.84	18.10	—		
In	0.008	—	2.219	456.4	273	16.21	1.57	3	24.30	—		

TABLE II  
 Values of the function  $D(y)$  interpolated for the temperatures of interest in liquid metals.

Liquid Metal	$\theta_{PY}/T_M$	$D^{T_M}(y)$	$\theta_{PY}/1.25T_M$	$D^{1.25T_M}(y)$	$\theta_{PY}/1.5T_M$	$D^{1.5T_M}(y)$	$\theta_{PY}/2T_M$	$D^{2T_M}(y)$
Li	1.3831	0.5755	1.2370	0.6112	1.1294	0.6392	0.9778	0.6806
Na	0.6835	0.7655	0.6113	0.7894	0.5577	0.7986	0.4840	0.8303
K	0.4451	0.8376	0.3981	0.8590	0.3632	0.8705	0.3147	0.8496
Rb	0.2954	0.8936	0.2642	0.9045	0.2413	0.9125	0.2085	0.9240
Cs	0.2251	0.9182	0.2013	0.9265	0.1836	0.9329	0.1592	0.9417
Mg	0.5070	0.8288	0.4535	0.8403	0.4140	0.8533	0.3581	0.8722
Al	0.5355	0.8019	0.4790	0.8319	0.4372	0.8472	0.3786	0.8653
Zn	0.4167	0.8525	0.3726	0.8673	0.3402	0.8783	0.2946	0.8939
Ga	0.6191	0.7795	0.5537	0.8078	0.5051	0.8234	0.4377	0.8406
Pb	0.2721	0.9018	0.2434	0.9118	0.2222	0.9129	0.1924	0.9297
Tl	0.3684	0.8623	0.3295	0.8820	0.3009	0.8917	0.2602	0.9059
Sn	0.5570	0.8067	0.4982	0.8256	0.4638	0.9087	0.3934	0.8602
Cd	0.3094	0.8888	0.2767	0.9002	0.2527	0.9086	0.2190	0.9204
Cu	0.3233	0.8841	0.3615	0.8632	0.2640	0.9046	0.2287	0.9170
Au	0.2908	0.8952	0.3251	0.8834	0.2375	0.9139	0.2056	0.9250
Ag	0.3156	0.8867	0.2823	0.8982	0.2577	0.9068	0.2231	0.9189
Fe	0.3034	0.8908	0.2714	0.9020	0.2478	0.9103	0.2145	0.9219
Co	0.3245	0.8837	0.2902	0.8954	0.2650	0.9043	0.2294	0.9167
Ni	0.3055	0.8884	0.2732	0.9014	0.2494	0.9097	0.2160	0.9214
In	0.5977	0.7936	0.5346	0.8139	0.4886	0.8288	0.4230	0.8504

not identical. Firstly, Ujihara used a temperature independent  $\theta_D$  in the upper limit of the integral, while we use here a temperature dependent  $\theta_{PY}(T)$ . The details of the evaluation of the integral in (31) for  $\omega_c^l(T)$  are given in appendix 1, utilizing standard methods for integrating Debye-like functions. In Figure 1 we illustrate the liquid metal electron-liquid phonon

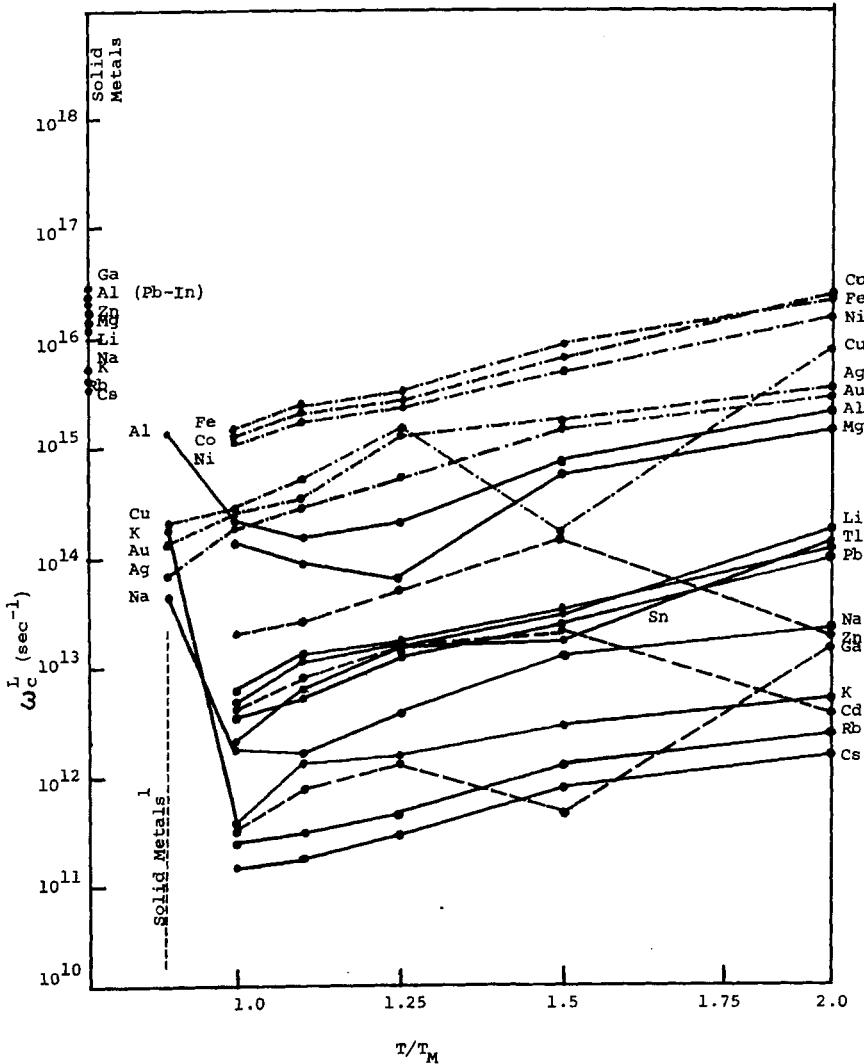


FIGURE 1 Electron-liquid phonon collision frequencies for twenty transition and non-transition liquid metals as a function of temperature above the melting temperature. Ujihara's electron-phonon collision frequencies in the solid metals are also shown.

TABLE III

Real and Imaginary parts of the dielectric constant and Reflectivity at three wavelengths and for temperatures at and above the melting temperatures

Liquid Metal	$\lambda = 10.6\mu, \omega = 1.78 \times 10^{14} \text{ sec}^{-1}$						
	$\epsilon_1^L(T_M)$	$\epsilon_2^L(T_M)$	$R^L(T_M)\%$	$\epsilon_1^L(2T_M)$	$\epsilon_2^L(2T_M)$	$R^L(2T_M)\%$	$R^L(1.5T_M)\%$
Li	- 6183	- 59.0	95	- 2475.0	- 850	92	93.5
Na	- 3412	- 32.0	93	- 3260.0	- 404	93	93
K	- 1779	- 4.0	91	- 1777.0	- 32	91	91
Rb	- 1497	- 68.0	90	- 1497.0	-1229	91	90.5
Cs	- 1217	- 0.5	89	- 1216.0	- 8	89	89
Mg	- 7977	-3590.0	96	- 64.0	- 876	88	91
Al	-15629	-7900.0	97	- 103.0	-1584	90	93.5
Zn	-18382	-7203.0	97	-18045.0	-1860	97	97
Ga	-29164	- 53.0	98	-29033	-1111	98	98
Pb	-33099	- 179.0	99	- 7844.0	-2703	96	97.5
Tl	-14564	- 334.0	97	- 9262.0	-4698	96	96.5
Sn	-24007	- 508.0	97	-12087.0	-8634	97	97
Cd	-13636	- 280.0	97	-13636.0	- 280	97	97
Cu	- 1370	-3012.0	93	- 3.0	- 206	76	84.5
Au	-1961	-1991.0	92	- 7.0	- 79	64	78.5
Ag	- 2910	-6224.0	95	- 12.0	- 346	81	88
Fe	- 114	-1063.0	88	- 0.6	- 61	48	68
Co	- 149	-1369.0	90	- 0.5	- 111	68	79
Ni	- 184	-5840.0	95	- 0.4	- 95	66	81.5
In	-18626	- 258.0	97	-14761.0	-5197	97	97

Liquid Metal	$\lambda = 1.06\mu, \omega = 1.78 \times 10^{15} \text{ sec}^{-1}$						
	$\epsilon_1^L(T_M)$	$\epsilon_2^L(T_M)$	$R^L(T_M)\%$	$\epsilon_1^L(2T_M)$	$\epsilon_2^L(2T_M)$	$R^L(2T_M)\%$	$R^L(1.5T_M)\%$
Li	- 61.0	- 107.0	70	- 60.0	- 7.	60	60
Na	- 33.0	- 56.0	61	- 33.0	- 0.7	50	50
K	- 17.0	- 66.0	61	- 17.0	- 0.06	37	37
Rb	- 14.0	- 0.002	33	- 14.0	- 0.02	33	33
Cs	- 12.0	- 0.0	29	- 11.0	- 0.02	29	29
Mg	- 116.0	- 8.0	69	- 41.0	- 209.0	76	68
Al	- 243.0	- 19.0	77	- 72.0	- 113.0	71	76
Zn	- 185.0	- 2.0	74	- 185.0	- 3.0	74	74
Ga	- 291.0	- 0.1	79	- 291.0	- 2.0	79	79
Pb	- 101.0	- 1.0	67	- 101.0	- 6.0	67	67
Tl	- 145.0	- 0.6	72	- 144.0	- 11.0	72	72
Sn	- 239.0	- 0.9	77	- 237.0	- 24.0	77	77
Cu	- 89.0	- 146.0	74	- 3.0	- 20.0	40	66
Cl	- 136.0	- 0.5	71	- 137.0	- 0.5	71	71
Au	- 87.0	- 128.0	72	- 6.0	- 15.0	36	60
Ag	- 88.0	- 13.0	65	- 11.0	- 30.0	49	62
Fe	- 53.0	- 50.0	63	- 0.6	- 6.0	18	40
Co	- 82.0	- 76.0	68	- 0.5	- 8.0	22	47
Ni	- 66.0	- 49.0	64	- 0.4	- 8.0	22	44
In	- 186.0	- 0.005	75	- 184.9	- 0.4	74	74

TABLE III (continued)

$$\lambda = 0.69\mu, \omega = 2.72 \times 10^{15} \text{ sec}^{-1}$$

Liquid Metal	$\epsilon_1^L(T_M)$	$\epsilon_2^L(T_M)$	$R^L(T_M)\%$	$\epsilon_1^L(2T_M)$	$\epsilon_2^L(T_M)$	$R^L(2T_M)\%$	$R^L(1.5T_M)\%$
Li	25	0.03	45	25.00	26.000	51	45
Na	14	0.01	24	13.00	15.000	40	33
K	7	0.002	19	7.00	8.000	27	27
Rb	5	0.0	16	5.00	0.006	16	24
Cs	4	0.002	12	4.00	0.004	12	19
Mg	49	0.02	55	27.00	25.000	52	56
Al	102	0.05	67	51.00	53.000	63	68
Zn	79	0.61	64	79.00	0.940	64	64
Ga	123.9	0.03	70	106.00	46.000	69	71
Pb	45	0.09	55	141.00	2.000	71	54
Tl	61	0.02	60	61.00	3.000	60	59
Sn	102	103.0	72	102.00	7.000	67	67
Cd	57	0.14	59	57.00	12.000	59	59
Cu	39	5.0	53	3.00	12.000	31	50
Au	37	5.0	52	6.00	15.000	36	50
Ag	38	4.0	52	10.00	17.000	40	51
Fe	31	19.0	51	0.60	4.000	10	43
Co	40	7.0	53	0.46	5.000	14	47
Ni	35	18.0	53	0.58	6.000	17	46
In	79	0.13	64	79.00	3.000	64	64

collision frequencies, as calculated using the Percus-Yevick collective coordinate model of a simple liquid, for  $T \geq T_M$  and Ujihara's  $\omega_c^e$  values for Al, Cu, K, Na, Ag and Au. For Na, K and Al we see  $\omega_c^e > \omega_c^L(T_M)$  while for Ag, Au and Cu we see  $\omega_c^e < \omega_c^L(T_M)$ , so that no definite conclusion can be drawn regarding whether our calculated collision frequencies in liquid metals are all on the high or low side due to the various approximations we have made. It seems that the collision frequency drops for non-transition metal liquids, and rises for transition metal liquids, but these are just a few examples to confirm this.

## 5 OPTICAL PROPERTIES OF THE LIQUID METALS AT HIGH TEMPERATURES

Table III illustrates  $\epsilon_1^L(T \geq T_M)$ ,  $\epsilon_2^L(T \geq T_M)$  and  $R^L(T \geq T_M)$  values calculated for twenty liquid metals. In Figures 2, 3 and 4 we illustrate  $R^L(T \geq T_M)$  at 0.69, 1.06 and 10.6 micron incident light wavelengths.

At 0.69 microns, we see that  $R^L$  is nearly constant in most non-transition metals, rises between  $T_M$  and  $1.5T_M$  in the alkali metals (Na, K, Rb, Cs), and falls severely in the transition metals (Ag, Au, Cu, Fe, Co, Ni). Pb seems to represent an anomaly, since it increases quite a bit for  $T > 1.25T_M$ .

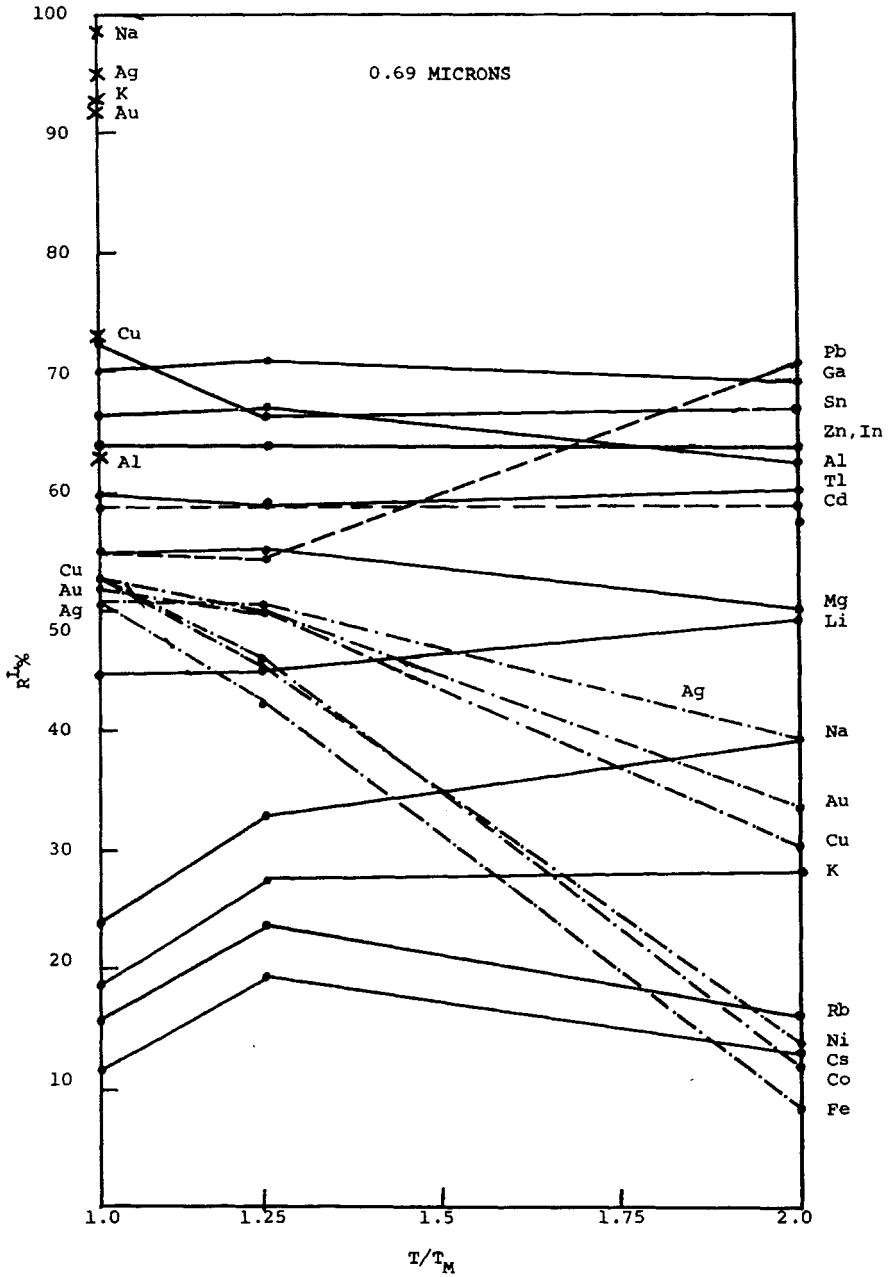


FIGURE 2 Reflectivity versus temperature for twenty liquid metals at 0.69 microns.

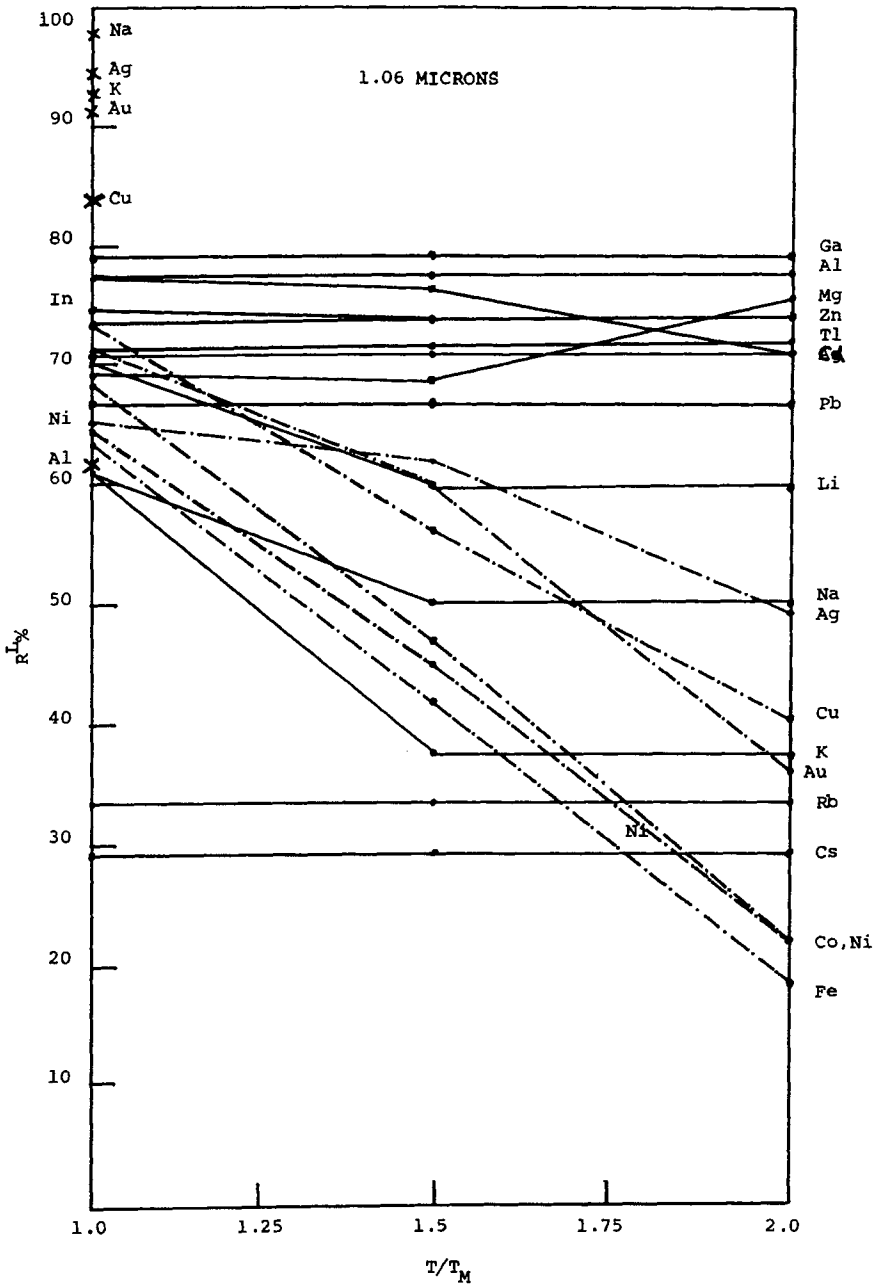


FIGURE 3 Reflectivity versus temperature for twenty liquid metals at 1.06 microns.



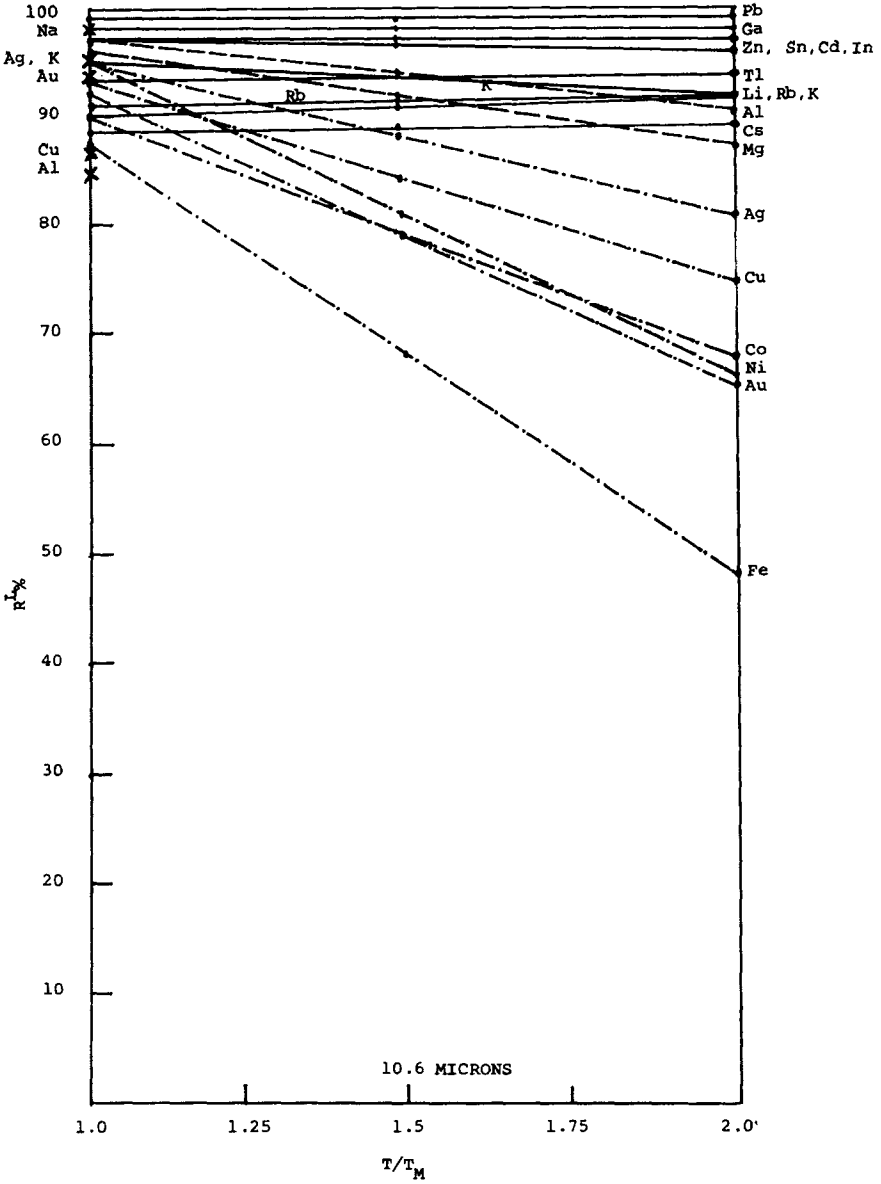


FIGURE 4 Reflectivity versus temperature for twenty liquid metals at 10.6 microns. In the latter three figures the reflectivity of the solid metals at the melting temperature is indicated by x's.

At 1.06 microns, all  $R^L$  values at  $T_M$  shift upwards, with respect to the  $R^L$  values at 0.69 microns, and at 1.06 microns the alkali metals experience a large drop in  $R^L$  for  $T$  between  $T_M$  and  $1.5 T_M$ . The other non-transition metals have a roughly constant  $R^L$  except for Mg and Al, which behave like Pb at 0.69 microns. The transition metals again have a large decrease in  $R^L$ , but less than they experienced at 0.69 microns.

At 10.6 microns, all  $R^L(T_M)$  values are shifted up to  $R^L \gtrsim 90\%$ . Of the non-transition metals, Al and Mg have some decrease in  $R^L$ , the alkali metals have a small  $R^L$  increase and the transition metals have a large  $R^L$  decrease at high temperatures, but never as much as at 0.69 microns since the initial  $R^L(T_M)$  is so much higher at 10.6 microns.

## 6 CONCLUSIONS

We conclude that, as Ujihara predicted in the solid metals, as the wavelength of the incident radiation increases from 0.69 to 10.6 microns, the reflectivity at any temperature for any liquid metal increases, and that the negative  $dR^S/dT$  continues as a negative  $dR^L/dT$  at any incident radiation wavelength. The liquid transition metals have a large negative  $dR^L/dT$ , as did Cu in Ujihara's treatment of  $dR^S/dT$ , while most other metals investigated have a negligible  $dR^L/dT$ . However, one metal presents an enigma. Al is predicted by Ujihara to have a larger negative  $dR^S/dT$ , larger even than that of Cu, and yet our calculations on liquid Al at all three wavelengths show that its  $dR^L/dT$  is much lower than those of all the transition metals, including Ag and Au also. Thus Al seems to be the only metal which shows a sharp change in  $dR/dT$  as the metal melts. If, as appears to be the case in the liquid metals, they split up into two groups in terms of their  $dR^L/dT$  slopes: transition metals and non-transition metals, we believe that they likewise should in the solid metals, so that Ujihara might have made an error in his calculation of  $R^S(T)$  for Al. This is further sketchily supported by Ujihara's own results, which show that non-transition metal  $dR^S/dT$  values (Li, Na) are far lower than transition metal  $dR^S/dT$  values (Cu, Ag, Au) in the solid state, with Al being the only high  $dR^S/dT$  non-transition metal.

Further thinking on this one discrepancy in the trends of  $dR^L/dT$  for twenty representative transition and non-transition metals indicates that the only possible explanation for the Al anomaly must be in the different constant values between our work and Ujihara's. If  $\omega_c^S(\text{Al}) = \omega_c^{L(\text{Fe, Co, Ni})}$  we could explain this, but  $\omega_c^{L(\text{Al})}$  is about half an order of magnitude lower, and  $\omega_c^{L(\text{Al})} \approx 10^{-1} \omega_c^{L(\text{Fe, Co, Ni})}$  for temperatures from  $T_M$  to  $2T_M$ . K and Na have a large  $\omega_c^L$  decrease, but  $\omega_c^{L(\text{Na, K})}$  is  $10^{-3} \omega_c^{L(\text{Fe, Co, Ni})}$ . So, if this were plausible as an explanation, Al should have a large discontinuity in  $R$  at  $T_M$  between the liquid and solid metal phases, and then little  $T$  dependence in the liquid

phase. While Al does exhibit this, so do Cu, Ag, Au, Na and K, and some of these latter are much larger, yet none of them exhibit a discontinuity in  $dR/dT$  at the phase transition. This reasoning for Al may still be valid though, since  $\omega_c$  drops upon melting do not along determine R, but relative  $\omega_p$  values estimated from the liquid and solid phase do also. Al has another anomaly, in that we find  $R^{L(Al)}(T_M) > R^{S(Al)}(T_M)$ , making  $dR/dT$  positive at  $T_M$  in contrast to all other metals treated. Again we think that the discrepancy in our calculated Q values, in contrast to those of Omini, indicates that these differences in R at the melting temperature are probably purely due to choice of input constants for the various metals, rather than actual phenomena, but a definitive answer to this question would require a detailed examination of the various constants used by Omini and Ujihara, which are unfortunately not present in their papers. The question of the abrupt discontinuity in  $dR/dT$  in Al still remains open, and we can only conclude that, since the solid and liquid metals both seem to split into the large negative  $dR/dT$  transition metals and the small negative  $dR/dT$  non-transition metals, none of which show a sharp discontinuity in  $dR/dT$  upon melting. Ujihara's predicted large temperature dependent reflectivity decrease is in error.

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## Appendix

We evaluate<sup>5</sup> the integral expression for  $\omega_c^L(T)$  in (T) in (31). We rewrite (31) as

$$\omega_c^L(T) = K^{1/2} T^5 I \quad (\text{A1})$$

where

$$I = \int_0^{\theta_{PV}/T} z^4 dz / (e^z - 1) \quad (\text{A2})$$

is a Debye integral. We integrate by parts, letting  $u = z^4$  and  $v = (e^z - 1)^{-1}$ , and using

$$\int_a^b u \, dv = uv \Big|_a^b - \int_a^b v \, du \quad (\text{A3})$$

to arrive at

$$I = z^4/(e^z - 1) \Big|_0^{\theta_{PY}/T} - 4 \int_0^{\theta_{PY}/T} z^3 \, dz/(e^z - 1) \quad (\text{A4})$$

The latter term is equal to

$$-4 M = -4 \theta_{PY}^2 D(y)/3 T^2 \quad (\text{A5})$$

where  $D(y)$  is tabulated, since, in the Debye theory of specific heat,

$$((U - U_0)/3RT)_{\text{Debye}} = D(y) = (3T^2/\theta_D^2) \int_0^{\theta_D/T} z^3 \, dz/(e^z - 1) \quad (\text{A6})$$

and, as we have stressed,  $\theta_D$  and  $\theta_{PY}$  are equivalent phonon parameters for their various states. Thus

$$L = ((\theta_{PY}/T)^4/(e^{\theta_{PY}/T} - 1)) - (4/3) D(y) (\theta_{PY}/T)^2 \quad (\text{A7})$$

and  $D(y)$  is tabulated in the literature.<sup>5</sup> We had to do some interpolation of the tabulated  $D(y)$  values since the  $y = \theta_D/T$  values did not correspond to the various fractions of  $\theta_{PY}/T$  required for this calculation (1/1.1, 1/1.25, 1/1.5, and 1/2.0).