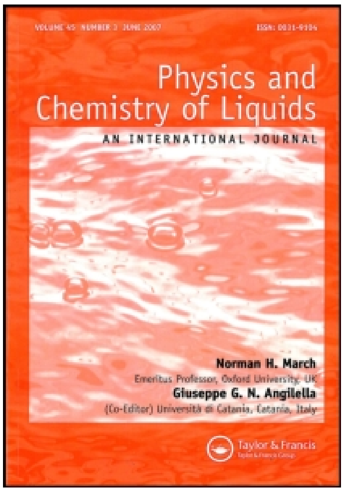

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A METHOD BASED ON RADIATIVE COOLING FOR DETECTING STRUCTURAL CHANGES IN UNDERCOOLED METALLIC LIQUIDS

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We introduce a structure-sensitive parameter for undercooled melts which can be measured in containerless processing experiments. We have established that the ratio, $R(T)$, of hemispherical total emissivity $\varepsilon_T(T)$ to constant-pressure specific heat $c_p(T)$ can serve as an indicator which is sensitive to any changes in short range atomic order in undercooled metallic melts. $R(T) \equiv \varepsilon_T(T)/c_p(T)$ values for nickel, zirconium, and silicon have been obtained using the high temperature electrostatic levitator while the levitated melts were undergoing purely radiative cooling into the deeply undercooled region. $R(T)$ plots for undercooled liquid nickel and zirconium indicate no significant change in short-range structure from their melting temperatures to 15% undercooling. In contrast, liquid silicon shows marked short-range structural changes beginning above its melting temperature and extending throughout the undercooled region. The short-range structure of liquid silicon is related to the highly-directional covalent bonding which characterizes its solid form.

The nickel and zirconium data show that ε_T varies linearly with T, in support of metal emissivity theories.

KEY WORDS: Short-range liquid structure, undercooled metals, nickel, zirconium, silicon, emissivity.

1. INTRODUCTION

In liquids, atoms which are separated by many interatomic spacings show little spatial correlation, while there exists on average a persistent spatial arrangement among atoms separated by shorter distances. It is the time-averaged persistent spatial arrangement of atoms over short distances which constitutes a liquid's short-range structure[1]. Peaks in pair distribution functions of liquid metals tend to become sharper as the temperature decreases[1,2]. But sharpening of the peaks is due to a reduction in the magnitude of thermal oscillations of atoms about their mean positions in the structure and it does not constitute a change in short-range structure. Rather, a change in short-range order means a substantial change in the atomic arrangement.

Two main types of structural changes which might occur as melts undergo temperature changes will be discussed in this paper: the glass transition exhibited by some pure metals and alloys, and the metallic-covalent bond transition exhibited by some semiconductors.

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The glass transition drastically affects a melt's thermal expansion coefficient, specific heat, and viscosity[3]; all three of which can be used as indicators of the glass transition. The metallic-covalent bond transition affects the viscosity, electrical conductivity, magnetic susceptibility, thermoelectric power, and thermal conductivity[4]. As discussed by Glazov *et al.*[4], all of these properties are particularly sensitive to this type of structural change.

The purpose of the present paper is to introduce a new parameter, $R(T) \equiv \varepsilon_T(T)/c_p(T)$, the ratio of the hemispherical total emissivity to constant-pressure specific heat, as an indicator which is sensitive to various kinds of structural transitions. Since $R(T)$ can be readily measured using non-contact techniques[5], it is particularly useful for assessing structural transitions in undercooled melts. In this paper we will discuss a general relationship between $R(T)$ and a metallic liquid's short-range structure taking undercooled liquid nickel, zirconium, and silicon as model samples.

2. LIQUID NICKEL AND ZIRCONIUM

If undercooled nickel and zirconium were to undergo any structural change, it would be limited to that associated with a glass transition. Therefore, this section discusses the relation between $R(T)$ and an approach to a glass transition.

2.1. *Behavior of Constant-Pressure Specific Heat During an Approach to a Glass Transition*

$c_p(T)$ values of liquid Bi, Sn, In, and Hg show a rise as the temperature decreases in the vicinity of the melting temperature[6], which indicates a substantial loss of interatomic holes[7], a phenomenon which ultimately causes the glass transition at T_g. On the other hand, liquid metals such as tungsten, rhenium, tantalum, molybdenum, niobium, iron, cobalt, nickel, copper, lead, and indium in the range of temperatures far above the glass transition temperature, i.e., $T >> T_g$, show a temperatue-independent c_p over a wide temperature range[8]. This is expected since the behavior of c_p for $T >> T_g$ is governed overwhelmingly by thermal vibrations of atoms while the energy associated with hole formation is negligible. In summary, for liquid metals whose only possible change in structure is that associated with a glass transition, c_p is constant if and only if the glass transition is not approached. On the other hand, c_p will increase with decreasing T if a glass transition is approached.

2.2. *Dependence of Electrical Resistivity on the Temperature of Metallic Melts*

The electrical resistivity $r_e(T)$ of liquid tungsten, rhenium, tantalum, molybdenum, niobium, iron, cobalt, nickel, copper, lead, and indium show a linear dependence on temperature over large temperature spans above T_m[8]. These data confirm the linear dependence predicted by quantum mechanical theory for both solid and liquid metals[9,10].

As seen above, an approach to a glass transition affects $c_p(T)$. But it probably does not affect the electrical resistivity $r_e(T)$ because the glass transition does not greatly affect the high-frequency thermal oscillations which determine r_e. This statement is supported by measurements on liquid bismuth. Liquid bismuth shows a clear rise in $c_p(T)$ as the temperature decreases from about 150 K above T_m to T_m, indicating an approach to a glass transition[6]. Yet $r_e(T)$ remains almost perfectly linear over that same temperature range[11]. This means that, if the glass transition is the only possible structural change of a metallic melt, r_e should show linearity with respect to the temperature even as a glass transition is approached.

2.3. *Behavior of Hemispherical Total Emissivity During an Approach to a Glass Transition*

We now turn our attention to the hemispherical total emissivity, $\varepsilon_T(T)$. The constant-pressure specific heat of undercooled liquid nickel is constant from T_m down to 14% undercooling[12]. Therefore, we can assume that, in that temperature range, undercooled nickel did not approach a glass transition. Figure 1 shows $R(T)$ normalized by its value at T_m. Since the plot shows a straight line for liquid nickel, constant $c_p(T)$ implies linear temperature dependence of $\varepsilon_T(T)$. Figure 2 shows the hemispherical total emissivity of liquid nickel assuming $c_p = 38.5$ J/mol/K[1]. $\varepsilon_T(T)$ in the figure is least-squares fitted by the expression $\varepsilon_T(T) = 0.0644 + 4.95 \times 10^{-5}\ T$

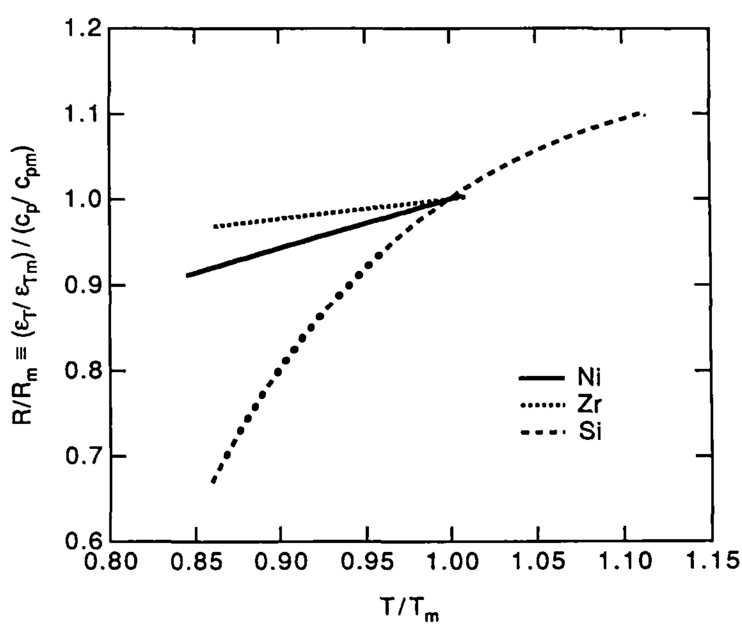

Figure 1 Experimentally-measured and normalized structure-sensitive parameter R/R_m vs. T/T_m for liquid nickel, zirconium, and silicon. The value of R/R_m at any given temperature is subject to a $\pm 5\%$ error. An equation for each curve is given in Table 2.

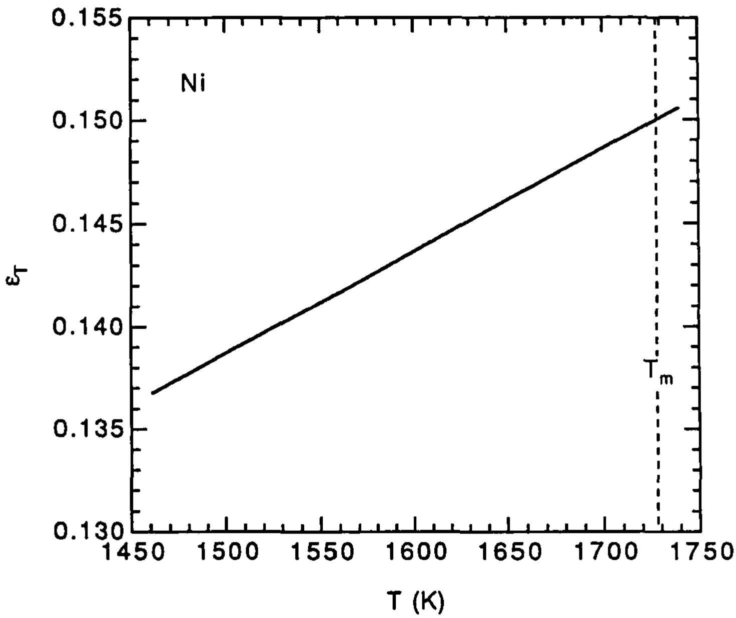

Figure 2 Hemispherical total emissivity vs. T for liquid nickel assuming $c_p = 38.5$ J/mol/K^1. The value at any given temperature is subject to a $\pm 5\%$ error.

with the uncertainty estimated to be $\pm 5\%$. Liquid emissivity data are not available for many materials, and to our knowledge Fig. 2 represents the only results for undercooled liquid nickel.

The fact that ε_T shows a linear temperature dependence is consistent with the theoretical result developed by Sievers[13] for solid metals which predicts a linear relationship between ε_T and r_e. Sievers began with expressions for a metal's spectral emissivity cast in terms of its frequency-dependent electrical conductivity. He integrated the spectral emissivity multiplied by Planck's expression for radiant emissive power over wavelength and angle to find to hemispherical total emissivity. Others have taken the same approach but Sievers' is presumably the most complete since it takes into account electron scattering at the surface and integrates over all wavelengths–not just the long wavelength limit treated by previous workers. The resulting expressions show that ε_T is linearly proportional to r_e. Although the linear law was proven to be accurate in experiments on solid copper[14], the applicability of Sievers' model to liquid metals and glasses may involve some caveats. More theoretical study of the emissivity of liquid metals would be helpful. Nevertheless, Sievers' model is supported by the present empirical results for liquid nickel.

According to Sievers' model and the present results for liquid nickel, $\varepsilon_T(T)$ depends linearly on $r_e(T)$. Therefore, we conclude that for liquid metals whose only possible change in structure is a glass transition, ε_T depends linearly on T regardless of whether a glass transition is approached.

Table 1 Properties of pure liquid nickel, zirconium, and silicon at their melting temperatures; T_m is the melting temperature, R is the ratio of hemispherical total emissivity to constant-pressure specific heat, and c_p is the constant-pressure specific heat.

Material	*Sample Mass (mg)*	$T_m(K)$	R_m	c_{pm} $(J/mol/K)$
Ni	19.4	1728	0.00389	38.5[1]
Zr	40.7	2128	0.00711	40.8[15]
Si	8.9 to 45.2	1687	0.00664	25.61[1]

Table 2 Curve fits to the experimentally-measured R/R_m vs. T/T_m; R/R_m is subject to a $\pm 5\%$ error.

Material	R/R_m	*Range of* T/T_m
Ni	$0.430 + 0.570\ T/T_m$	0.85 to 1.01
Zr	$0.770 + 0.230\ T/T_m$	0.86 to 1.01
Si	$1.18 - 323 \exp(-7.51 T/T_m)$	0.86 to 1.11

2.4. Behavior of R During an Approach to a Glass Transition

We have seen that an increase in $c_p(T)$ with decreasing T accompanies an approach to a glass transition, while $\varepsilon_T(T)$ depends linearly on T regardless of whether a glass transition is approached. As a result, we conclude that a liquid metal whose only possible structural change is that associated with the glass transition will exhibit constant dR/dT as long as a glass transition is not approached. The plot of $R(T) = \varepsilon_T(T)/c_p(T)$ should show a negative second derivative when a glass transition is approached. This is the reason for plotting $\varepsilon_T(T)/c_p(T)$ rather than $c_p(T)/\varepsilon_T(T)$; the former gives an easily-recognizable straight line when a glass transition is not approached, or a curved line when a glass transition is approached.

2.5. Results for Undercooled Nickel and Zirconium

Table 1 shows the properties of liquid nickel and zirconium. Table 2 shows the results of radiative cooling experiments. We have already concluded that since $c_p(T)$ of liquid nickel is constant, no change in short-range liquid structure occurs over the temperature range $1.01T_m > T > 0.85T_m$. This is to be expected since $T >> T_g$.

Figure 1 and Table 2 show that $R(T)$ varies linearly with T for liquid zirconium. On the basis of the above discussion we can conclude that the short-range liquid structure remains unchanged from the melting temperature to 15% undercooling. Again, this is expected since $T >> T_g$. In liquid zirconium, $c_p(T)$ is constant and $\varepsilon_T(T)$ varies linearly with T as shown in Fig. 3. Assuming $c_p = 40.8$ J/mol/K[15], $\varepsilon_T = 0.223 + 3.13 \times 10^{-5}\ T$ over $0.86T_m < T < 1.01T_m$, where T is in K. The uncertainty is estimated to be $\pm 5\%$. To our knowledge no other hemispherical total emissivity data are available for undercooled liquid zirconium.

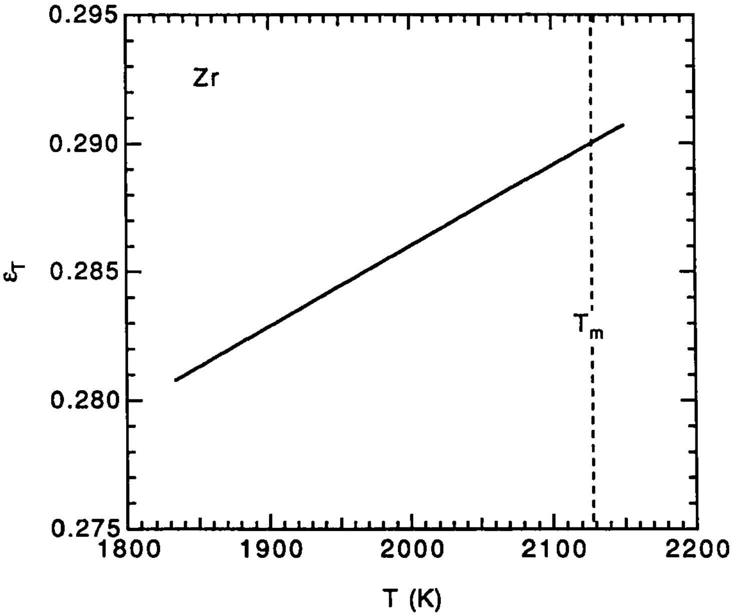

Figure 3 Hemispherical total emissivity vs. T for liquid zirconium assuming $c_p = 40.8$ J/mol/K[15]. The value at any given temperature is subject to a $\pm 5\%$ error.

3. LIQUID SILICON

Changes in atomic bonding are known to occur in liquid silicon in the vicinity of its melting temperature[4]. Therefore, in order to investigate the structure of undercooled silicon we must examine the effect of atomic bonding on $R(T)$.

According to Glazov *et al.*[4], silicon is metallic in the liquid state because its electrical conductivity is high and decreases with increasing T. The short-range liquid structure mimics body-centered cubic packing and has a coordination number of eight. Solid silicon is a semiconductor with the diamond cubic structure. The structure forms a relatively open network of tetragonal units with coordination number four. The solid bond is covalent, and electrons lie in the highly-directional sp^3 hybridized orbitals.

As liquid silicon cools, covalent bonds begin to form in the predominantly metallically-bonded melt. The presence of the covalent bonds can be sensed by their effect on the kinematic viscosity. A plot of $\ln(\nu s)$. $1/T$ for liquid silicon shows a straight line with positive slope for temperatures greater than about 1480 °C[4]. At lower temperatures, however, ν increases more rapidly with decreasing T. As discussed at length in Glazov *et al.*[4], the rapid increase in ν with T is due to the formation of covalent bonds. A decrease in the coordination number accompanies the emergence of covalent bonds. In effect, the short-range liquid structure gradually takes on characteristics of the solid before actual solidification takes place. One should expect a change in $c_p(T)$ to accompany the emergence of strong covalent bonds; $c_p(T)$ should increase with decreasing T.

The emergence of covalent bonds might also be expected to influence r_e for two reasons. First, electrons entering covalent bonds are no longer available for conduction; this is evidenced by the fact that the electrical resistivity of solid silicon is about 20 times that of liquid silicon when both quantities are measured at the melting temperature[4]. Second, the average coordination number around a covalently-bonded atom decreases relative to a metallically-bonded atom, thereby affecting the distribution of atoms through which electrons must travel; according to Ziman's formula, the change in short-range structure directly influences electrical resistivity[16]. The direction in which r_e changes due to the combined effects is not immediately clear. Furthermore, measuring r_e of liquid silicon is difficult. The available data are only for $T > T_m$ and show a significant amount of scatter[4]. The data quality is not sufficient to discern whether r_e deviates from linearity. All things considered, however, the emergence of covalent bonds is expected to cause r_e to deviate from a linear dependence on T. As discussed in Section 2.3, a deviation of r_e from a linear dependence on T should cause a deviation of ε_T from a linear dependence on T. Therefore, emergence of covalent bonds is expected to cause $\varepsilon_T(T)$ to deviate from a linear dependence on T.

In principle, the affects of $c_p(T)$ and $\varepsilon_T(T)$ could cancel, thereby rendering $R(T)$ insensitive to changes in the liquid's atomic bonding. But it is much more likely that the combined affects of $c_p(T)$ and $\varepsilon_T(T)$ are to cause $R(T)$ to deviate from a linear dependence on T when atomic bonding changes take place in the liquid. Therefore, we conclude that constant dR/dT indicates that most likely no structural changes are underway. On the other hand, non-constant dR/dT indicates that changes in atomic bonding are definitely underway.

Table 1 shows the properties of liquid silicon while Table 2 shows the results of the radiative cooling experiments. Figure 1 and Table 2 show R/R_m for liquid silicon. It is non-linear over the entire range of temperature tested: from $1.11T_m$ to $0.86T_m$. Note that the data to which the curves in Fig. 1 were fit showed considerable amounts of scatter[5]. The choice of an exponential fit for liquid silicon was somewhat arbitrary. It is certain, however, that a gradual change in atomic bonding occurred in liquid silicon as it cooled. In the light of the $R(T)$ data we conclude that as liquid silicon cools, covalent bonds begin to emerge substantially above T_m. The structure continues to evolve to at least $0.86T_m$, where solidification in the present experiments occurred.

4. OTHER STRUCTURAL CHANGES

In order to use $R(T)$ as a structure-sensitive parameter, it is necessary to assess the effect of each type of structural change involved. We have discussed an approach to a glass transition and the emergence of covalent bonds as two typical structural changes which affect $R(T)$. It might be possible to imagine a change in short-range structure that does not change c_p but it is much more likely that the conversion of one short-range structure to another would be accompanied by significant changes in c_p. Similarly, it might be possible to imagine a change in short-range structure that does not affect $r_e(T)$–but it is much more likely that the conversion of one short-range structure to another would be accompanied by a change in $r_e(T)$. In summary, a liquid metal with constant dR/dT most likely has unchanging short-range structure, while a liquid metal with varying dR/dT definitely has a temperature-dependent short-range structure.

5. CONCLUSIONS

It was demonstrated for liquid metals that a deviation of the ratio $R(T) \equiv \varepsilon_T(T)/c_p(T)$ from a linear dependence on T indicates that a change in short-range structure occurs. The ratio $R(T)$ was measured for liquid nickel, zirconium, and silicon over a wide range of temperatures including the undercooled region using electrostatic levitation in vacuum. The results indicate that undercooled nickel and zirconium show no sign of structural changes over the temperature range $1.01T_m > T > 0.85T_m$. This result is expected since $T >> T_g$ for both Ni and Zr over the temperature range. The results also show that $\varepsilon_T(T)$ increases linearly with T for both liquid nickel and zirconium. For liquid silicon, however, $R(T)$ indicates that a change in short-range structure occurred during radiative cooling. The change in structure is associated with the emergence of covalent bonds in an otherwise metallically-bonded melt. Undercooled silicon's short-range structure continues to evolve down to at least $0.86T_m$, where solidification occurred.

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