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Metal-to-Semimetal Transition in Supercooled Liquid Silicon

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Computer simulations, using the Stillinger-Weber potential, have previously been employed to demonstrate a liquid-liquid transition in supercooled silicon near 1060 K. From calculations of electronic structure using an empirical psuedopotential, we show that silicon undergoes an associated metal to semimetal transition with a resistivity jump of roughly 1 order of magnitude. We show that the electronic states near the Fermi energy become localized in the low temperature phase, and that changes in electronic structure between the two phases arise from a change in atomic structure, and not from a change in density.

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Silicon is an element of technological importance, and of interest at a fundamental level, particularly in the crystalline and amorphous forms. In addition to the liquid-to-crystal transition occurring around $T_f = 1685$ K, another first order *liquid to amorphous* transition $\sim$250 K below T_f (in the supercooled liquid) has been inferred from experimental data [1–3]. Subsequent experiments at ambient [4,5] and high pressures [6], as well as computer simulations [7–9], support the occurrence of such a transition. In particular, recent computer simulations [9] using the Stillinger-Weber (SW) potential [10] demonstrate the transition to be a *liquid-liquid transition*, as indeed suggested by Aptekar [3]. The inference, thus, is that amorphous *solid* silicon is thermodynamically contiguous with the *low temperature* liquid [below the liquid-liquid (LL) transition], while the liquid at the freezing transition is thermodynamically continuous with the supercooled liquid above the LL transition.

There has been considerable interest in LL transitions in single component substances [11], proposed and studied extensively in recent years, e.g., for water [12,13], silica [14], carbon [15], and phosphorus [16]. Brazhkin *et al.* [17] have interpreted large changes in electronic conductivity in iodine, selenium, and sulfur at high pressures to be due to LL phase transitions. Amorphous silicon (*a*-Si) is a semiconductor, while liquid silicon near T_f is a metal [18]. It is thus of interest to study changes in conductivity and electronic structure of silicon with temperature in the supercooled liquid, and, in particular, those occurring at the LL transition. We address these questions in this Letter, by using atomic coordinates generated by molecular dynamics (MD) simulations of $N = 512$ silicon atoms [9] employing the Stillinger-Weber (SW) potential [10].

The SW potential is a classical empirical potential with two and three body terms [10], energetically favoring tetrahedral coordination of the atoms. At zero pressure, SW silicon displays a freezing transition close to the experimental temperature of 1685 K, and a LL transition at $T_{\rm LL} = 1060$ K [7–10] which underestimates the experimental value of $\sim$1400 K. The density and coordination number change discontinuously at $T_{\rm LL}$. In the present work, we study the electronic structure at $T = 1055$, 1082, 1258, 1510, and 1711 K, analyzing up to five configurations at each temperature, sampled from MD simulations ranging from a few ns to 60 ns in length. Of these temperatures, $T = 1055\ {\rm K} < T_{\rm LL}$ and $T = 1711\ {\rm K} > T_f$.

For the electronic structure calculation, we use a model pseudopotential [19] $V_{\rm Si}$ which approximates the total potential seen by valence electrons. We avoid the more elaborate density functional theory (DFT) calculations in view of (i) the high computational cost and (ii) the underestimation of the band gap in DFT calculations. A comparison with DFT calculations is described later. The Hamiltonian we use is

$$H = T + \Sigma_i^N V_{\rm Si}(\vec{r} - \vec{d}_i), \qquad (1)$$

where T is the kinetic energy and $\vec{d}_i$ is the position of the ith atom. $V_{\rm Si}$ is based on (a) the empirical potential fit by Cohen and Heine to optical data [19] ($V_{\rm OP}$) and (b) the Heine-Abarenkov pseudopotential [20,21] ($V_{\rm HA}$) for the long wavelength part, both of which were reported in $\mathbf{q}$ (momentum) space. Pseudopotentials similar to ours have been employed with success in electronic structure calculations of a variety of liquids [22,23], notably liquid carbon [23]. $V_{\rm OP}$ is available only for $q/(2k_F) > 0.5$ ($k_F = 0.9590\ {\rm bohr}^{-1}$ being the Fermi wave vector), which we smoothly interpolate with $V_{\rm HA}$ for $q/(2k_F) < 0.5$. Our choice, thus, combines the accurate band gap estimation of (a) with the analytical form of (b) for long wavelengths. We truncate our potential for $q > q_c$ [$q_c/(2k_F) = 1.26$], equivalent to a scattering length of roughly half the Si-Si bond length. The resulting model pseudopotential is (see Fig. 1)

$$V_{\rm Si}(q) = V_{\rm HA}(q), \qquad q < k_F V_{\rm Si}(q) = V_{\rm OP}(q),$$
$$k_F < q < q_c V_{\rm Si}(q) = 0.0, \qquad q > q_c. \qquad (2)$$

This choice of potential allows the use of a plane-wave basis set with an energy cutoff of 69 eV to represent

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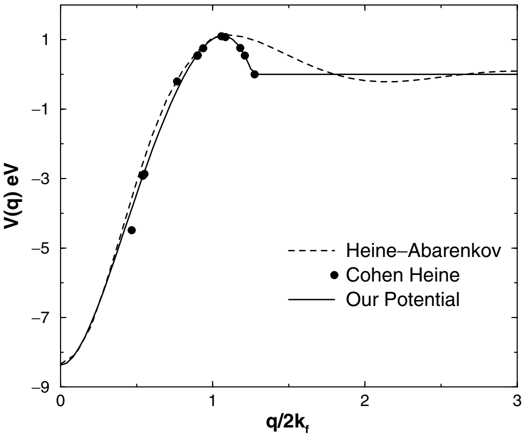

FIG. 1. Comparison of our modified pseudopotential with the Heine-Abarenkov pseudopotential. Also shown are the Cohen-Heine empirical fits to optical data.

electron wave functions (roughly 14 000 plane waves per state of the 512 atom system). We obtain a band gap of 0.92 eV for crystalline silicon in the diamond structure, which compares well with the experimental value of 1.1 eV. We use the preconditioned conjugate gradient method [24] to diagonalize the Hamiltonian. In order to calculate the conductivity, we obtain states with energies at least $10k_BT$ above the Fermi energy E_f. We use eight Monkhorst-Pack [25] (MP) points in sampling the Brillouin zone (BZ) of the 512-atom supercell, which amounts to sampling the BZ for the diamond structure with a $12 \times 12 \times 12$ MP mesh. Figure 2 shows the density of states (DOS) obtained at different temperatures. The DOS remains essentially unchanged from $T = 1711$ K to $T = 1258$ K. A small dip in the DOS at E_f is apparent for $T = 1082$ K, just above the transition. For $T = 1055$ K, just below the transition, the dip in the DOS at the Fermi energy is dramatic. The DOS deviates significantly at other energies as well, compared to the DOS at higher temperatures. The DOS remains finite at the E_f. However, conductivity depends not only on the DOS near E_f, but also on the degree to which the electronic states are localized. We therefore calculate the DOS as a function of both the energy and a measure of localization, the inverse participation ratio (IPR), defined [26] as

$$\mathrm{IPR}(\psi_n) = M \frac{\sum_i^M [|\psi_n(r_i)|]^4}{\{\sum_i^M [|\psi_n(r_i)|]^2\}^2} \tag{3}$$

where i runs over the M real space mesh points, and ψ_n is the wave function for a given band n. IPR $= M$ for fully localized states and IPR $= 1$ for a fully extended state. Figure 3 shows the density of states as a function of energy and IPR for two temperatures. At $T = 1082$ K (and at higher temperatures; data not shown), all states display roughly the same, low IPR, indicating that all states are extended. In contrast, at $T = 1055$ K, states near the Fermi energy show markedly larger IPR, indicating a greater degree of localization. We may thus expect the conductivities for these two cases to be significantly different.

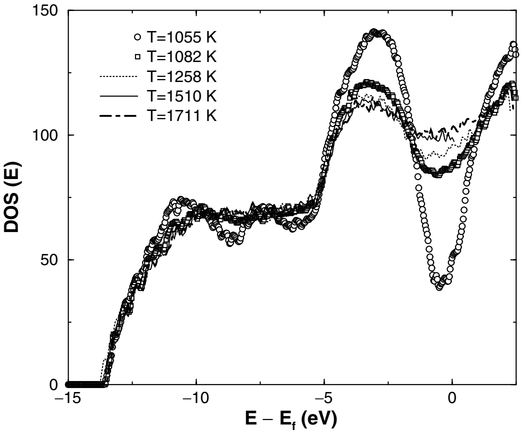

FIG. 2. The electronic density of states (DOS) is shown for various temperatures analyzed. A pseudogap is seen for $T = 1055$ K (just below the LL transition). The DOS at higher temperatures approaches the free electron form, reflecting the observed metallic behavior. The Fermi energies are 11.21 eV (1055 K), 11.83 eV (1082 K), 12.1 eV (1258 K), 12.05 eV (1510 K), and 11.99 eV (1711 K).

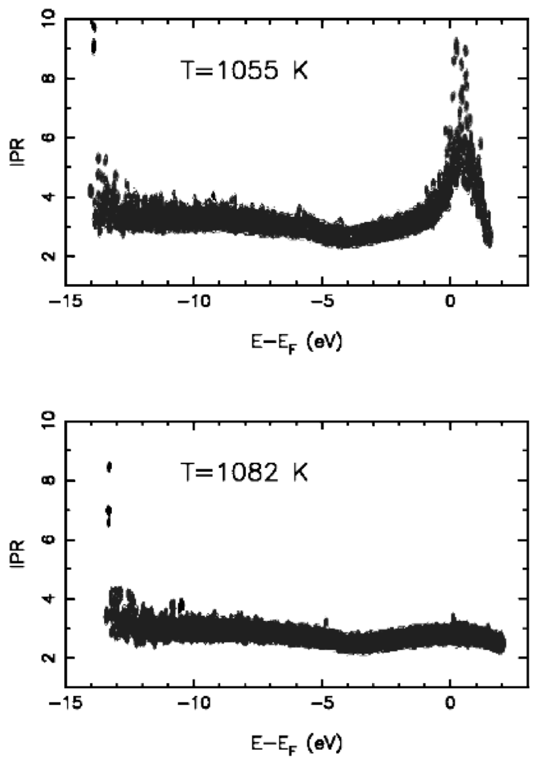

FIG. 3. Contour plot of the density of states (DOS) as a function of IPR(ψ_n) and energy for one configuration each at $T = 1055$ and $T = 1082$ K. The IPR for $T = 1082$ K remains essentially unchanged as a function energy, and is small, indicating that all states extended. For $T = 1055$ K, states near the Fermi energy are seen to display a marked increase in IPR.

We calculate the frequency-dependent electrical conductivity $\sigma(\omega)$, using the Kubo formula [27], as previously done for liquid [28] and amorphous [26] silicon:

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2 V\omega} \sum_{i,k} (f_i - f_k)|\vec{M}_{i,k}|^2 \delta(E_k - E_i - h\omega), \tag{4}$$

where e is the electron charge, V is the volume of the system, ω is the frequency, and f_i is the Fermi-Dirac occupation probability at electron energy E_i. Matrix elements $\vec{M}_{i,k} = \langle\psi_i|\vec{P}|\psi_k\rangle$ (where $\vec{P}$ is the momentum operator) are easily calculated in the plane-wave basis. The dc conductivity is found by extrapolation to $\omega = 0$. Resistivities $\rho(\omega)$, shown in Fig. 4 for four temperatures, vary slowly with T between $T = 1711$ and $T = 1082$ K, while for $T = 1055$ K the resistivity is significantly larger. We find the dc resistivity at $T = 1711$ K to be in the range of 70–80 $\mu\Omega$ cm which agrees very well with the experimental dc resistivity at 1740 K, in the range of 77–83 $\mu\Omega$ cm [18]. Our calculation yields better results than earlier methods for liquid Si [28]. In the low temperature phase ($T = 1055$ K), the dc resistivity is in the range 800–850 $\mu\Omega$ cm, values typical of semimetals (e.g., graphite has a dc resistivity of 783 $\mu\Omega$ cm). The resistivity at $T = 1082$ K is 120 $\mu\Omega$ cm which is comparable to that in metals, albeit on the higher end. The LL phase transition thus involves a roughly 1 order of magnitude jump in the resistivity, which may be termed a metal to semimetal transition. Extrapolation of experimental data for a-Si in the range of 400 °C to 60 °C [29], yields resistivities (0.66–3.3 Ω cm) which are higher by 3 orders of magnitude than calculated values for the low T liquid. We believe the difference to arise from the coordination number of 4.2 found for the low T liquid, higher than the a-Si value of 4. Such a discrepancy may arise either because the low T liquid structure is not predicted satisfactorily by the SW potential or because, in reality, the liquid structure is distinct from a-Si.

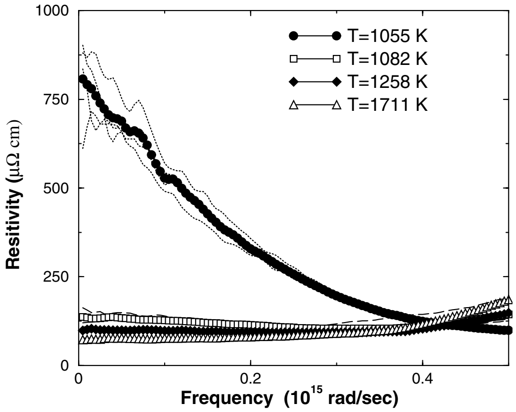

FIG. 4. Plot of resistivity vs frequency for $T = 1055$, 1082, 1258, and 1711 K, showing a significant change in resistivity between $T = 1082$ and $T = 1055$ K. Thin lines (clearly visible only for $T = 1055$ K) correspond to individual configurations, and thick lines with symbols are averages for each temperature.

The density of the liquid jumps from 0.0524 above, to 0.0494 atoms per Å^3 below, the LL transition [30]. The structure of the liquid also changes, as reflected, e.g., in the distribution of coordination number, whose average changes from 4.2 at $T = 1055$ K to 4.61 at $T = 1082$ K, while the fraction of four-coordinated atoms changes from about 83% at $T = 1055$ K to about 43% at $T = 1082$ K [31]. To determine the relative importance of density and structural changes to electronic structure, we calculate the electronic structure for two additional atomic configurations obtained (i) by rescaling atomic coordinates for a $T = 1055$ K configuration, to produce a configuration whose density equals that of the liquid at $T = 1082$ K, and (ii) by rescaling coordinates for a $T = 1082$ K configuration to produce a configuration whose density equals that of the liquid at $T = 1055$ K. The DOS for these configurations, shown in Fig. 5 alongside the DOS for the original configurations, shows that a change in density itself, without structural change, has marginal effect on the electronic DOS. We conclude that the marked change in the electronic DOS at the LL transition arises primarily from a change in liquid structure, rather than a change in density.

Since the coordination number of the liquid in the studied T range changes from 4.2 to 5.12, the reliability of the pseudopotential we use, based on data for four-coordinated crystalline silicon, needs further validation. To this end, we calculate the DOS, and resistivities for liquid configurations of 64 atoms for $T = 1082$, 1258, 1510, and 1711 K using our pseudopotential and *ab initio* DFT based on norm-conserving pseudopotential [32]. The DOS using the two methods agrees reasonably (data not shown), but the DFT bandwidths are typically 8%–10% smaller, and, as remarked earlier, the

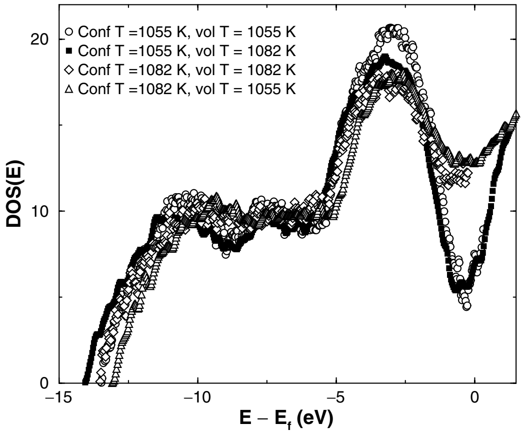

FIG. 5. Density of states for: ○, a $T = 1055$ K configuration; ■, the same $T = 1055$ K configuration, but with coordinates scaled so that the density equals that at $T = 1082$ K; ◇, a $T = 1082$ K configuration; △, the same $T = 1082$ K configuration, but with coordinates scaled so that the density equals that at $T = 1055$ K.

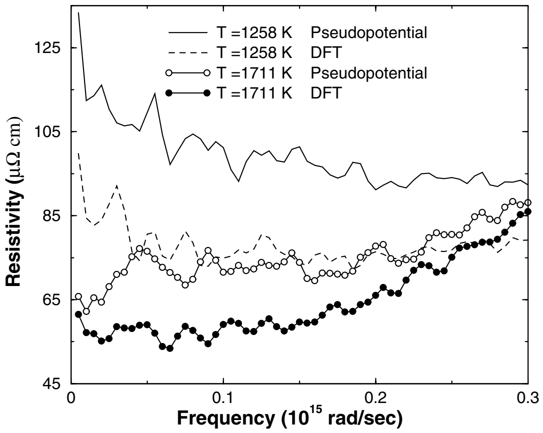

FIG. 6. Plot of resistivity vs frequency for $T = 1258$ and $T = 1711$ K, calculated using the pseudopotential, and using DFT.

pseudo-band-gap is underestimated by DFT. Figure 6 shows the resistivities from the two methods for $T = 1258$ and 1711 K, which are in moderate agreement for $T = 1711$ K, and a much poorer agreement at $T = 1258$ K. Since the liquid shows greater tetrahedral structure at $T = 1258$ K, we conclude that the disagreement between pseudopotential and DFT calculations is due to the underestimation of the band gap by DFT rather than due to non-four-coordinated geometry. This supports our expectation that the electronic structure itself is not so sensitive to the potential, and its structure dependence can be captured well with a structure factor along with a reasonable potential [33].

In summary, we have demonstrated a metal to semimetal transition in supercooled silicon, accompanying the LL transition previously found. The resistivity of the liquid changes by about 1 order of magnitude at the transition. Our analysis indicates the cause of the change in electronic properties to be the change in liquid structure rather than the density.

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[30] The quoted densities are for 1055 and 1082 K, respectively. The lowest temperature above the LL transition at which a liquid was equilibrated in the present study was 1060 K, where the density is 0.052 07 atoms per Å^3.

[31] The percentage of atoms displaying 3, 4, and 5 coordination (where a distance cutoff of 0.293 nm is used) are, respectively: 0.268, 82.8, and 16.1 for $T = 1055$ K; 0.74, 42.9, and 46.7 for $T = 1082$ K; 2.36, 28.9, and 47 for $T = 1711$ K. The concentration of dangling bonds (associated with three coordinated atoms), at low temperatures where they may be expected to play a significant role, is minimal, and would not have a substantial influence on the conductivity changes.

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