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Effects of subconduction band excitations on thermal conductance at metal-metal interfaces

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Increased power densities combined with the decreased length scales of nanosystems give rise to large thermal excitations that can drastically affect the electron population near the Fermi surface. In light of such conditions, a model is developed for electron thermal boundary conductance (eTBC) that accounts for significant changes in the electron and hole populations around the Fermi level that occur at heightened temperatures. By including the contribution of subconduction band electrons to transport and evaluating the transmission coefficient based upon the total number of available states, an extension of eTBC predictions to high temperatures is made possible. © *2010 American Institute of Physics*. [doi:10.1063/1.3276908]

In multilayer metallic films, electrical transport properties are perturbed by electron scattering off of the altered periodic potential at an interface.[1] This scattering creates a resistance to all electronic transport, including the thermal boundary conductance of the electrons (eTBC). Electron driven interfacial thermal transport is not often addressed, however, as most studies of the phenomenon focus on conduction of the phonons instead.[2] This focus, in turn, has resulted in methods that provide relatively accurate predictions of the phonon TBC via the diffuse mismatch model (DMM),[3] or some variation of it,[4–6] without the need for intense computational rigor. Using a similar approach applied to electrons, recent work has shown that the thermal conductance at a metal-metal interface is well described by an electronic DMM (EDMM), thereby providing a relatively quick and accurate prediction of the eTBC.[7]

The electronic TBC is a critical parameter for a variety of high heat flux applications in metal systems including micro/nanoprocessing via ultrashort pulsed machining, control of laser melting, and film disintegration rates on metal surfaces.[8,9] For each of these processes, the high heat fluxes involved result in greatly elevated electron temperatures that may reach in excess of 10 000 K before diffusive phonon scattering is capable of cooling the system creating energy and momentum loss by the electrons. At these electron temperatures, significant Fermi smearing occurs allowing for subconduction band electrons to participate in the thermal transport. Previous demonstrations of the EDMM, however, were restricted to relatively low electron temperatures. In response, we derive the EDMM in a general form to allow for prediction of electron TBC at higher temperatures. Specifically, the aluminum/copper (Al/Cu) interface is examined over a large temperature range in order to examine the effects of *d*-band electron excitations on electronic thermal interface conductance, h_e, in high heat flux applications.

Assuming an isotropic metal, the eTBC across the metal 1/metal 2 interface is given by

$$h_{e,12} = \frac{1}{4}\int_0^\infty (\varepsilon - \varepsilon_{F,1}) D_1(\varepsilon) \frac{\partial f_1}{\partial T} v_{F,1} \zeta_{12} d\varepsilon, \tag{1}$$

where ε is the electron energy, D is the density of states (DOS), f is the electron distribution function, T is the electron temperature, v_F is the Fermi velocity, ζ is the transmission coefficient, and $\varepsilon_{F,1}$ is the Fermi energy of metal 1. As in any analytical treatment of interfacial thermal transport, the critical parameter is the transmission coefficient that defines the ratio of energy reaching the interface that is capable of forward scattering across the boundary. Assuming the metals are in equilibrium at the interface, an electron forward scattered at the boundary will move from occupied state, k, in metal 1 to empty state, k', in metal 2 as a consequence of the Pauli exclusion principle. Quantifying the likelihood of this event is made possible by equating the flux between the electrons on side 1 and the holes on side 2 while assuming diffusive scattering, i.e., $\zeta_{12}(\varepsilon) = 1 - \zeta_{21}(\varepsilon)$. These assumptions lead to a statement of detailed balance[1] given by

$$\int_0^\infty (\varepsilon - \varepsilon_{F,1}) D_1(\varepsilon) f_1 v_{F,1} \zeta_{12}(\varepsilon) d\varepsilon = \int_0^\infty (\varepsilon - \varepsilon_{F,2}) D_2(\varepsilon)(1 - f_2) v_{F,2} \zeta_{21}(\varepsilon) d\varepsilon. \tag{2}$$

To evaluate Eq. (2), it is necessary to define the energy scale describing the interfacial system as a whole. In order to follow as closely as possible the original work of Gundrum *et al.*,[7] we begin by assuming that the materials' Fermi energies are equivalent on an absolute scale. This assumption arises as a manifestation of detailed balance, which requires that the entire electron system maintain thermal equilibrium at the metal-metal interface.[10] For convenience, we then define $\varepsilon_{F,Al}$ to be the reference energy for our system. With knowledge of the reference energy, the Fermi level of the entire system may be specified based upon the properties of aluminum via $\varepsilon_{F,Al} = \varepsilon_{F,1} = \varepsilon_{F,2} = 11.63$ eV.[11]

After specifying the energy scale, Eq. (2) is simplified by consideration of only elastic scattering processes, i.e., a tran-

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sition from state k to k' will not result in a change of energy—resulting in the following expression:

$$\zeta_{12}(\varepsilon) = \frac{D_2(\varepsilon)(1-f_2)v_{F,2}}{D_1(\varepsilon)f_1 v_{F,1} + D_2(\varepsilon)(1-f_2)v_{F,2}}. \quad (3)$$

In the limit of low temperatures, Eq. (3) reduces to the form of the transmission probability presented by Gundrum *et al.*,[7] and the EDMM becomes

$$h_{e,12} = \frac{1}{4}\zeta_{12}(\varepsilon_F)D_1(\varepsilon_F)v_{F,1}\int_0^\infty (\varepsilon-\varepsilon_F)\frac{\partial f_1}{\partial T}d\varepsilon$$

$$= \frac{\pi^2}{12}k_B^2 T\frac{D_2(\varepsilon_F)v_{F,2}}{D_1(\varepsilon_F)v_{F,1} + D_2(\varepsilon_F)v_{F,2}}. \quad (4)$$

Further simplification allows Eq. (4) to be rewritten as

$$h_{e,12} = \frac{1}{4}\frac{\gamma_1 \nu_{F,1}\gamma_2 \nu_{F,2}}{\gamma_1 \nu_{F,1} + \gamma_2 \nu_{F,2}}T, \quad (5)$$

which is the final form of the EDMM derived by Gundrum *et al.*[7] In Eq. (5), γ is the low temperature constant of electron heat capacity, or the Sommerfeld parameter. At low temperatures (i.e., around room temperature), the EDMM agrees well with experimental data (as shown by Gundrum *et al.*),[7] justifying the diffusive assumption in this temperature range. As temperature increases, the thermal de Broglie wavelength will decrease making the electron wavelength smaller with respect to the electronic density, thereby increasing the probability of diffusive scattering in the high temperature range investigated in this study.

While Eq. (5) is limited to low temperatures, Eq. (1) utilized in conjunction with Eq. (3) represents a general form of the EDMM. This generalized form allows for extension to higher temperatures where subconduction band electrons may contribute to the transport such as the case in noble metals where d-band excitations influence transport.[12–14] To then investigate this high temperature regime, the Al/Cu interface is considered in detail. At low temperatures, Cu is a free electron metal and h_e can be accurately modeled with the low temperature theory discussed above. However, at electron temperatures of ~3000 K, Fermi smearing causes thermal excitations from the high-number density $3d^{10}$ band to energies above the Fermi level creating a drastic change in the thermal properties.[14] Aluminum, on the other hand, has no d-bands and can be treated as a free electron metal over a large temperature range (up to, at least, 20 000 K).[14]

To calculate h_e in the high temperature limit, we first approximate the Al DOS with a parabolic conduction band of the form

$$D_c(\varepsilon) = \frac{3N_c}{2\varepsilon_F}\sqrt{\frac{\varepsilon}{\varepsilon_F}}, \quad (6)$$

where the subscript c refers to the conduction band and N_c is the free electron number density, which for Al is $N_c = 18.06 \times 10^{28}$ m^{-3}.[11] The conduction band of Cu is also approximated by Eq. (6) only with $N_c = 8.45 \times 10^{28}$ m^{-3} and the energy spectrum shifted by $\varepsilon_{F,Al} - \varepsilon_{F,Cu}$ to account for the equating of the Fermi levels on an absolute scale with $\varepsilon_{F,Cu} = 7.0$ eV.[11] This causes the conduction band DOS in Cu to take the form $D_c(\varepsilon) = 3N_c\sqrt{(\varepsilon - 4.63)}/(2\varepsilon_{F,Cu}^{3/2})$. In the case of large thermal excitations where Fermi smearing excites electrons in the d-bands to the conduction band, the subbands of Cu must be taken into account as well.[14] In this case, the DOS of Cu is described by $D_{Cu}(\varepsilon) = D_c(\varepsilon) + D_d(\varepsilon)$ where D_d is the DOS of the $3d^{10}$-band and can be approximated by a Gaussian distribution in energy space centered at $\Gamma_0 = 3.1$ eV below the Fermi energy with a full-width-half-maximum of $\Gamma = 3$ eV.[15,16] Therefore, the magnitude of the DOS of the 3d band of Cu is approximated by

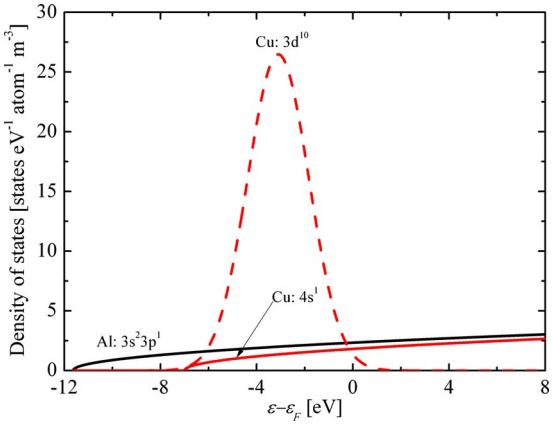

FIG. 1. (Color online) DOS of Al and Cu as a function of energy relative to the Fermi energy. Since metal composites in equilibrium must have the same Fermi energy, we shift the Cu DOS so that the Fermi energy aligns with Al. The s- and d-band in Cu are shown separately for clarity.

$$D_d(\varepsilon) = \frac{0.94}{\Gamma}N_d \exp\left\{-2.77\left[\frac{\varepsilon - (\varepsilon_{F,Al} - \Gamma_0)}{\Gamma}\right]^2\right\}, \quad (7)$$

where N_d is the electronic number density of the $3d^{10}$ band in copper which is the number of electrons in the $3d^{10}$ orbital times the atomic number density of Cu, yielding $N_d = 8.45 \times 10^{29}$ m^{-3}. Figure 1 shows the DOS of Al and Cu as a function of energy relative to the Fermi energy.

Once the form of the DOS is known for Cu and Al, the chemical potential for each material must be evaluated as the electrons are described by the Fermi distribution, $f = \{1 + \exp[(\varepsilon - \mu)/k_B T]\}^{-1}$, where μ is the temperature dependent chemical potential. The chemical potential is determined by evaluating

$$N = \int_0^\infty D(\varepsilon) f d\varepsilon \quad (8)$$

and iterating μ at each temperature until the total electron number density, N, becomes the constant value for the material of interest ($N_{Al} = 18.06 \times 10^{28}$ and $N_{Cu} = 9.3 \times 10^{29}$ m^{-3}). Specifics of this procedure for Cu including the Cu d-bands are discussed in detail in the Refs. 13, 14, and 16.

With the appropriate parameters now defined, the eTBC is evaluated using Eq. (1) with the transmission coefficient given by Eq. (3). The TBC predictions for a flux of electrons in Al crossing an Al/Cu interface and for a flux of electrons in Cu crossing a Cu/Al interface are shown in Fig. 2(a). Also shown in this figure is the prediction using Eq. (5) extended to high temperatures. For calculations of Eq. (5), we use the theoretically determined value for γ for Al (91.2 J m^{-3} K^{-1}), since our calculations assume Al has a perfectly parabolic conduction band. For copper, on the other hand, the experimentally determined value for γ for Cu (96.8 J m^{-3} K^{-2}) is utilized as the assumption of a perfectly parabolic conduction band does not account for the small electron density from the $3d^{10}$ bands that are available at the Fermi energy

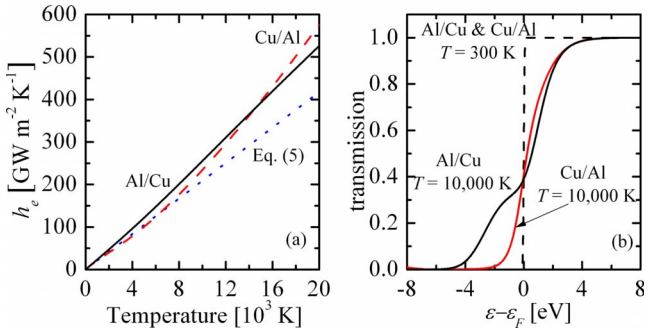

FIG. 2. (Color online) (a) TBC predictions for a flux of electrons in Al crossing an Al/Cu interface (Al/Cu) and for a flux of electrons in Cu crossing a Cu/Al interface (Cu/Al). Also shown in this figure is the prediction using Eq. (5) extended to high temperatures. The eTBC clearly deviates from the linear trend predicted from the low temperature theory as temperature increases. At intermediately high temperatures, the eTBC from Cu/Al is lower than h_e from Al/Cu due to the large number of holes in the Cu *d*-band. Much greater temperatures, however, cause greater transport from Cu to Al as the great number of electrons participating in the transport mitigates their lower transmission probability. (b) Transmission probability as a function of energy for the cases shown in (a) for T=300 and 10 000 K. At 300 K, the transmission probabilities are nearly identical since only states around the Fermi energy are available and Cu and Al have similar shaped Fermi surfaces. In contrast, as temperature is increased to introduce holes in the Cu *d*-band, the number of available states for transmission of the Al thermal flux increases near the maxima of this *d*-band.

(see Fig. 1). The previous form of the EDMM [Eq. (5)] does not account for these subconduction band contributions to the transport as it is, again, derived only for low temperatures. As such, this form of the EDMM also does not account for the temperature dependence of the chemical potential.

In spite of these differences, calculations of h_e using each method converge to a linear trend at low temperatures consistent with the original EDMM theory. The current predictions, in contrast, clearly deviate from this linear trend as temperature increases due to the consideration of the subconduction band electrons. For a majority of this temperature increase (1000 to 14 500 K), the TBC of electrons moving from Cu to Al is lower than that of transport from Al to Cu. At first glance this is rather unintuitive as the thermal flux of electrons in Cu is much higher than that in Al due to the large population of *d*-band electrons excited in Cu. However, eTBC is not determined solely by the thermal flux in the material, but also by the transmission probability at the interface. The transmission probability [Eq. (3)], meanwhile, is governed by both the number of electrons reaching the interface as well as the number of available (i.e., empty) states in the material on the complementary side of the boundary. For example, as temperature increases sufficiently to initiate the excitement of *d*-band electrons to the Fermi surface in Cu, electrons from the Al can transmit their energy across the interface and fill the large number of now empty *d*-band states. On the other hand, at these temperatures when electron flux originating from Cu is incident upon Al, there are not enough empty states in Al to accommodate transmission causing both a lower transmission probability and eTBC.

To illustrate this, the transmission probability is shown as a function of energy for temperatures of 300 and 10 000 K in Fig. 2(b). At 300 K, the transmission probabilities are nearly identical since only states around the Fermi energy are available and Cu and Al have similar shaped Fermi surfaces. Yet as temperature is increased, the number of holes in the copper greatly escalates due to the excitement of the *d*-band. Thus, the number of available states for transmission of the Al electrons into Cu increases as well resulting in a "hump" in the transmission ratio near the maxima of the *d*-band DOS and a higher resultant eTBC. The influence of the different transmission probabilities becomes mitigated at higher temperature (i.e., $T>14\,500$ K), however, as number of electrons participating in the Cu becomes overwhelming, nearly an order of magnitude greater than that in the Al. Even with a lower probability of transmission, the much greater flux eventually causes the eTBC of electrons moving from Cu to Al to become greater than that of the complement. Hence, the transport must be viewed in light of not only the probability of forward scattering but also the relative balance between the numbers of carriers and empty states in each material.

In conclusion, a model is developed to predict electron TBC across a wide temperature range. This is made possible by developing a more generalized form of the EDMM that includes contributions from electrons that are thermally excited from subconduction band energies. To demonstrate the applicability of the approach, example calculations are shown for Al/Cu interfaces at temperatures where *d*-band electrons are thermally excited in Cu. These temperature regimes, and the resulting predictions the eTBC, are extremely relevant for short pulsed laser heating applications in thin metal composite films often used in laser machining and melting processes.

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