Anomalous Thermionic Emission of Some Borides and Carbides of Rare Earth and Transition Elements*

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Thermionic emission constants, A^*, up to several thousand times larger than the A_0 (120 amp/cm^2—°K^2) predicted theoretically for metals have been reported for several compounds involving transition metals and rare earths with boron and carbon. It is suggested that such anomalously large emission constants, as well as some anomalously small ones, are due to the relatively large distances between metal atoms as a result of which the energy bands originating from the incomplete atomic f and/or d sublevels are narrow enough for nondegeneracy to occur in the experimental temperature range.

THE thermionic emission reported for UC, a UC—ZrC solid solution,[1] ThC, ZrB,[2] CeB_6, PrB_6, and NdB_6[3] is anomalous in the sense that the parameter A^* obtained by fitting the data to an expression having the form of the Richardson-Dushman equation,

$$j=A^*T^2\exp(-W/kT), \quad (1)$$

is larger than A_0, the theoretical maximum of 120 amp/cm^2—°K^2 (work function, W, assumed constant and all other symbols have their standard meanings). Values of A^* larger than A_0 can be justified theoretically on the assumption of a temperature dependent work function, $W=W_0-aT$. A^* is then $A_0(1-r)\exp(a/k)$, where r is the reflection coefficient for electrons passing through the surface. Wigner[4] showed that for simple metals $\exp(a/k)$ could range between approximately 10^{-2} and 10^2. Although the majority of the values of A^* [1-3] fall within the range delineated by the above-mentioned limits on $\exp(a/k)$, those for UC, the UC—ZrC solid solution and perhaps ZrB do not, that reported for UC being particularly high, 7.3×10^5 amp/cm^2—°K^2.

As the list above indicates, high values of A^* seem to be associated with compounds of rare earth and transition metals with nonmetals like boron and carbon. Inasmuch as the metal atoms in such compounds are spaced rather far apart, the overlap of the orbitals corresponding to the incomplete f and/or d subshells is probably small, a condition favoring the existence of narrow energy bands. The suggestion is therefore prompted that the anomalous thermionic emission stems from the extreme narrowness of the energy bands, because of which the degeneracy temperature of the electron gas is low enough to lie in or near the temperature range in which the emission is measured.

Calculations by Lehman[5] for Th and U and by Ridley[6] for U provide a picture of the band structure of uranium in which a relatively wide $6d$ band overlaps a narrow $5f$ band, the $7s$ and $7p$ levels being raised so high upon formation of the solid that they are most likely unoccupied. According to Ridley the width of the $6d$ band is ~6 ev while that of the $5f$ band is $\sim\frac{1}{2}$ to 1 ev wide. Spin-orbit coupling tends to split each band into a pair of sub-bands. Data on the electronic specific heat of α-U at low temperatures[7] indicates the density of states at the Fermi-level, $N(E_0)$, to be 2.3 states/atom-ev which is consistent with the order of magnitude of the calculated width of the $5f$ band.[6] A very similar picture probably holds for α-Pu in which, however, the $5f$ band is probably narrower while the sub-bands are better separated.

The electronic specific heat of α-Pu[8] is around a hundred times larger than that of a simple metal. This corresponds to a density of states at the Fermi-level of 10.4 states/atom-ev and an effective electronic mass ratio (m^*/m) of around a hundred. With a mass ratio of this magnitude an electron gas containing of the order of 10^{23} electrons/cm^3 would become nondegenerate above ~1000°K. Thus, in UC where the distance between uranium atoms is considerably larger than the average nearest neighbor distance in either α-U or α-Pu the conditions seem to be particularly favorable for a narrow band structure.

To test the hypothesis that the large values of A^* reported for UC and other compounds are due primarily to the narrowness of the energy bands, the Fermi-level of a simple rectangular band (separated by many kT from the nearest vacant energy levels) was calculated as a function of temperature. The Fermi-level, ζ, was found to be roughly proportional to kT, the coefficient increasing rapidly as the band is filled. For a band of width kT and 0.9 occupied, $\zeta\approx3kT$.

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Since the equation for the thermionic current may be written as

$$j=A_0 \exp(\zeta/kT)T^2 \exp(-|W_0|/kT), \qquad (2)$$

where W_0 is the energy at the lower edge of the band relative to the vacuum, it is apparent that the narrow band can indeed be responsible for observed A^* values much greater than A_0.

It should be noted, however, that when a narrow band is less than about half occupied ζ is of opposite sign, the coefficient increasing rapidly as the occupancy of the band decreases to zero. Thus, A^* can be considerably smaller than A_0.

It is interesting to consider the manner in which the thermionic emission parameters A^* and W vary with progression through the series of $4f$ rare earth hexaborides. These compounds are isomorphic, all having very nearly the same unit cell dimensions. The metal atoms, separated by distances ranging between 4.10 and 4.16 A for the various members of the series, lie in the interstices of a simple cubic framework which has regular octahedra of boron atoms at its lattice points.[9] The work function, W, rises with increasing atomic number of the metallic constituent, reaches a maximum for EuB_6 and drops in a discontinuous fashion at GdB_6.[9,10] Samsonov attributes the way in which W varies along the series to the progressive filling of an energy band (the lower $4f$ spin sub-band), the sudden drop occurring because a higher band has begun to be occupied after the lower one has been filled.[9,10] According to the picture presented above A^* should, therefore, increase to values well above A_0, reach a maximum at EuB_6, and then drop suddenly to a value much smaller than A_0 for GdB_6. While there are no published A^* values available for PmB_6 or SmB_6[9] this type of behavior seems indeed to occur; A^* increases from 73 amp/cm^2—°K^2 for LaB_6 to ~5000 amp/cm^2—°K^2 for EuB_6 and falls to 0.8 amp/cm^2—°K^2 for GdB_6.[9]

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