ANOMALOUS LOW-TEMPERATURE SPECIFIC HEAT OF GOLD

Douglas L. Martin
Division of Pure Physics, National Research Council, Ottawa, Canada
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The specific heat of 99.9999% pure gold has been measured in the temperature ranges 0.4-1.5°K and 3-30°K, and the smoothed results are shown as a plot of Debye temperature (θ^C) in Fig. 1. These results should be contrasted with the normally observed initial decrease of θ^C with increasing temperature.

In view of the unexpected nature of the present results the apparatus was immediately checked by measuring pure copper, in the same calorimeter, in the range 3 to 30°K. Results in good agreement with those previously reported[1] were obtained.

The results below 1.5°K were analyzed on the assumption (not strictly correct) that they could be represented by the sum of terms linear and cubic in temperature. In this manner an electronic specific heat coefficient (γ) of 174.1 ± 4.3 μcal/(°K)^2-(g atom) and a low-temperature limiting Debye temperature (θ_0^C) of 162.4 ± 2.0°K were found. (The error limits are 95% confidence limits.) The θ_0^C value is in excellent agreement with the θ_0^{el} value of 161.6°K obtained from elastic constant measurements at low temperatures.[2] Previous specific heat measurements on gold[3,4] had led to θ_0^C values of about 165°K, as do the present results if they are fitted to terms linear and cubic in temperature in the range 1 to 4°K. Thus the earlier discrepancy between θ_0^C and θ_0^{el} values for gold was due to the assumption of a "T^3 region" in the specific heat extending to relatively high temperatures.

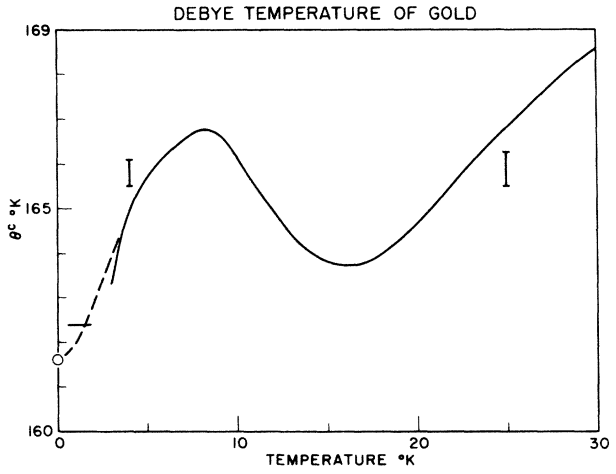

FIG. 1. The Debye temperature of gold. Solid lines represent smoothed experiment results, the point at 0°K is calculated from elastic-constant results, and the dashed line is a suggested interpolation. The vertical bars represent the effect of a 1% change in specific heat, the electronic specific heat being assumed to remain constant.

The observed maximum in the θ^C plot presumably corresponds to a region in the lattice vibration spectrum where the density $f(\nu)$ is increasing less rapidly than the square of the frequency. Further experimental investigation of this point would be possible by other techniques such as neutron scattering. The possibility that the lattice specific heat might vary in the manner found for gold has been discussed theoretically by Bhatia and Horton[5] (and others[6,7]) in terms of relations between the elastic constants. However, on this theory copper would be more likely to show anomalous effects than would gold. This discrepancy might be due to the admitted approximations in the theory or might indicate that some other explanation must be sought. For instance, it has been suggested[8] that discontinuities in the electron-phonon interaction, associated with the Fermi surface, might result in anomalous dispersion relations and this idea has been extensively discussed.[9] There is also the possibility of an anomalous electronic specific heat; the above discussion has assumed this to vary linearly with temperature in the usual way.

The specific heat of copper appears to be quite normal,[1] and the present work shows the specific heat of gold to vary anomalously with temperature. Accurate specific heat measurements on silver, the intermediate metal in the periodic classification, would therefore be of considerable interest—particularly since a wide range of electronic specific heat coefficients have been reported for this metal[10] suggesting the possibility of anomalous specific heat. It is proposed to make such measurements before reporting in detail on the present work.

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HIGH-TEMPERATURE ANNEALS OF QUENCHED GOLD*

R. M. Emrick
Department of Physics, University of Arizona, Tucson, Arizona
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It is generally observed that quenched-in lattice vacancies in gold anneal near room temperature by forming clusters and, to a much lesser extent, by moving to dislocations. Theoretical[1] and experimental[2,3] estimates of the divacancy binding energy range from 0.1 eV to 0.4 eV. Thus, it is usually impossible to observe single vacancies moving to a fixed number of sinks under ordinary experimental conditions. Rarely have first-order kinetics been observed for quenches even from 700°C. Data on the loss of vacancies during quenches as a function of quenching rate have been interpreted in terms of a first-order process by Meshii et al.[4] They observed that at high temperatures the probability per jump of reaching a sink times the entropy factor, which they refer to as the sink density, is several orders of magnitude less than that observed in anneals carried out near room temperature. It would therefore appear that at high temperatures, vacancies are annealing to pre-existing sinks and not forming clusters.

In the present experiment, 0.005-inch diameter 99.999% pure gold wires supplied by Sigmund Cohn were quenched from the vicinity of 875°C into water. The specimen was then placed in an oil bath held at 27.80 ± 0.02°C where it remained throughout the experiment. A negligible amount of background anneal occurred at this temperature during an experiment. The specimen was pulse-heated to the vicinity of 300°C for periods of 40 to 80 msec by means of a shaped electrical current pulse. The rise and decay times of the temperature pulses were about 1 msec and the majority of the pulses were flat-topped to ±10°C. Temperature was recorded photographically by simultaneously observing the current through and the voltage across the specimen with a dual-beam oscilloscope. Sensitivity was such that the temperature could be determined to ±3°C. Temperature along the 3-cm gauge length was found to be uniform to this degree by observing relative voltage drops at a number of 0.001-inch potential leads spot-welded along the gauge length of a specimen identical to the one used in the experiment. A series of pulses was made at one temperature and another series at a temperature about 35°C higher. The resistance remaining after each pulse was measured by a standard bridge technique.

Temperature-time plots, Fig. 1, were made for each pulse. The time for each pulse was normalized to a constant annealing temperature by a weighting factor $\exp[-(E_m/k)(1/T_0 - 1/T_m)]$, where T_0 is the normalized temperature, T_m the measured temperature of the curve segment being weighted, and E_m the vacancy migration energy. The effective time was usually changed by less than 10%.

The resulting $\Delta\rho/\Delta\rho_0$ vs t values were plotted

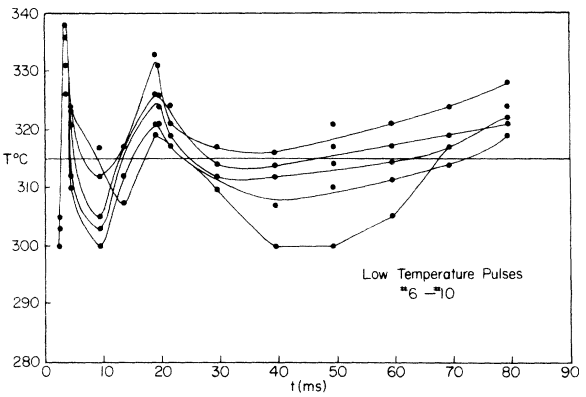

FIG. 1. Pulse temperature as a function of time for a group of pulses. Mean temperature was taken to be 315°C.