gated empirically by Montgomery et al.[7] The dimensions of the components comprising the gasket and the orientation and shape of the sample contained in the gasket considerably influence the pressure distribution and, without calibration, it cannot be assumed that the pressure on the sample is the load applied to the anvils divided by their face area. Montgomery et al. report that at room temperature a radial pressure gradient exists in the sample cavity. Consequently, a fine wire sample bent into the arc of a circle is utilized so that the sample will lie on an isobar. A series of experiments described below were done to establish the pressure calibration and to demonstrate that a sufficiently hydrostatic pressure is attained.

For the ordering experiments, a sample of Cu₃Au wire of 0.010-in. diam. is bent into a circular arc 0.125 in. in diameter and then flattened by rolling to a thickness of 0.007 in. The composition of this wire as determined by chemical analysis is 50.13 wt % Cu and 49.85 wt. % Au. Stochiometric wire would be 49.17 wt. % Cu. For pressure calibrations, samples of bismuth wire ($D=0.003$ in.) and lead wire ($D=0.007$ in.) were used. The current and potential leads to the sample are pure iron wires 0.004 in. in diameter. These are brought out of the sample chamber between the two lavite gaskets. Electrical leads of lower-strength material are broken off when pressure is applied. In addition to the electrical leads, two Chromel–Alumel thermocouples are placed in the sample cavity. One, placed in contact with the specimen, serves to measure its temperature; the other activates a temperature controller. Before use, the thermocouples are calibrated against a certified, standard couple. After being pressurized several times the couples retain their calibration; this is taken as evidence that they are not significantly cold worked during pressurizing.

To attain high temperature the entire anvil assembly is heated by a surrounding electric furnace and by heaters built into the anvil support blocks.

Pressure Calibration

A calibration at room temperature was made by placing a bismuth wire in the space ordinarily occupied by the Cu₃Au sample. The I–II transition was found to occur at an indicated pressure (load on the anvils divided by bearing area) of 24.6±1 kbar. This is to be compared with the accepted transition pressure of 25.5 kbar.[8] A calibration at high temperature was made by observing the pressure-dependence of the melting point of lead. Lead wire was substituted for the sample and its resistance observed at constant pressure as the temperature was raised at a rate of 5°C per minute. The onset of melting was indicated by an erratic be-
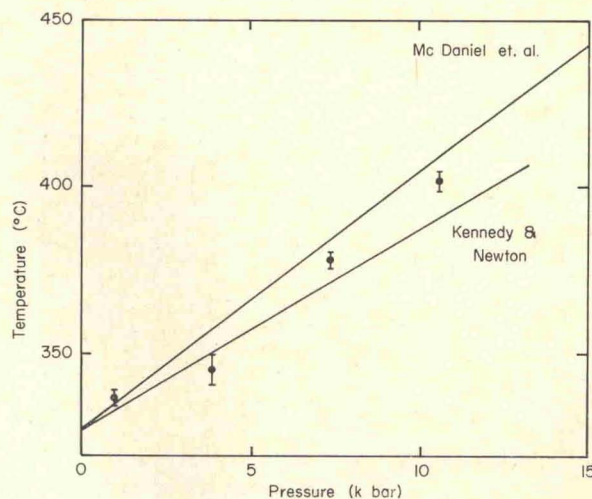

FIG. 3. Observed melting temperature of lead as a function of indicated pressure in the Bridgman anvil device.

havior of the resistance apparently associated with flow of liquid lead along the current and potential leads. That melting had actually occurred at this point was verified by inspection of the sample heated to successively higher temperatures; the flow of the liquid was clearly seen under a low-power microscope when the anvil assembly was taken apart. The melting temperature at several indicated pressures is shown in Fig. 3. For comparison, the melting curves of lead determined by McDaniel, Babb, and Scott[9] (extrapolated) and by Kennedy and Newton[10] are shown.

From the results of these experiments it was concluded that, to within the reproducibility attained with the anvil apparatus, it suffices to take the actual pressure as equal to the indicated pressure.

That the pressure generated with the composite gasket assembly shown in Fig. 2 is sufficiently hydrostatic for ordering experiments is demonstrated by comparing the resistance changes in a cold-worked sample of Cu₃Au held at constant pressure and slowly heated with the changes in an annealed sample treated the same way. The annealed sample shows a steady increase of resistance with temperature due to disordering and to the thermal component of the resistance; the previously cold-worked sample shows a resistance decrease as the cold work is annealed out under pressure and then shows the same resistance-temperature behavior as the initially annealed sample.

THE CRITICAL TEMPERATURE FOR ORDERING

The order–disorder transformation in Cu₃Au is of the first order, i.e., is characterized by a discontinuity in the volume and entropy at the critical temperature,

[7] P. Montgomery, H. Stromberg, G. H. Jura, and G. Jura, in *High Pressure Measurement* (Butterworths Scientific Publications, Ltd., London, Washington, 1963), p. 1.

[8] G. Kennedy and P. LaMori, in *Progress in Very High Pressure Research*, F. P. Bundy, W. R. Hibbard, Jr., and H. M. Strong, Eds. (John Wiley & Sons, Inc., New York, 1961), p. 304.

[9] M. L. McDaniel, S. Babb, and G. J. Scott, J. Chem. Phys. **37**, 822 (1962).

[10] G. Kennedy and R. C. Newton, in *Solids Under Pressure* W. Paul and D. Wanschaeur, Eds. (McGraw-Hill Book Company, Inc., New York, 1963), p. 163.
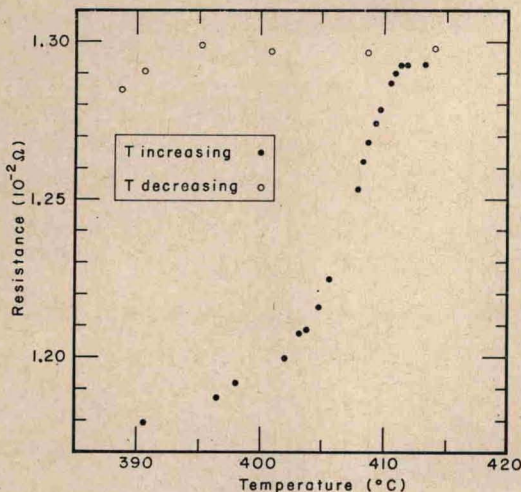
FIG. 4. Resistance of Cu₃Au wire during heating and subsequent cooling through T_c at a pressure of 10.5 kbar.

T_c, above which long-range order no longer exists. As an ordered alloy is heated, the long-range order decreases slowly and continuously until T_c is reached at which temperature the remaining long-range order vanishes. The critical temperature can be conveniently observed by means of resistivity measurements: If the sample is heated slowly and is at a uniform temperature throughout, there will be a discontinuity in the resistance vs temperature curve at T_c. Determination of T_c is made most effectively by a heating curve; when the disordered alloy is cooled through T_c considerable supercooling is often observed.

To find the change in T_c in Cu₃Au under pressure, slow heating experiments were performed on ordered wire samples. In most of the experiments the sample was first subjected to pressure and then heated, but in a few cases the sample was held at 300 bars and then heated to 200°C before the desired pressure was applied. In the latter case the sample would be subjected to smaller stress gradients during application of pressure. Equally satisfactory results were obtained by both methods, indicating again that the deviator stresses within the sample chamber are too small to influence the ordering behavior. After pressure is attained, the samples are heated at the rate of 20°C/h from 200°C to about 450°C; near T_c the heating rate is 0.3°C/min or less. Investigation at 1-atm pressure of the effect of heating rate on the observed value of T_c indicates that for the rate employed here, no measurable superheating occurs. Results of a typical experiment are shown in Fig. 4. From curves of this kind T_c is determined to within ±1°C. While holding the sample near T_c the following procedure can be used to determine whether or not T_c has been exceeded: The sample is held at constant temperature and its resistance observed as a function of time. If the resistance decreases with time the sample has not disordered, since the resistance decrease is indicative of

continued antiphase domain growth, a relatively slow process at all temperatures below T_c. With these techniques it is found that $T_c = 389 \pm 1$°C at $P = 300$ bars, a pressure low enough so that the shift in T_c is less than 1°C. A determination of T_c on the same sample material immersed in a fluid at 1 bar gave 388 ± 2°C, indicating that good accuracy is attained in the temperature measurements in the anvils. The experimental results of Hanneman and Strong[11] show no significant change in the calibration of Chromel–Alumel thermocouples in the pressure range of our experiments.

The observed values of T_c at various pressures are shown in Fig. 5. The initial slope of the curve of T_c vs P can be found from Clapeyron's equation, $dT/dP = T_c V_t / H_t$, where V_t is the volume change and H_t the enthalpy change at the critical temperature. The transformation volume at 1-atm pressure is known from the high-temperature x-ray-lattice parameter measurements of Keating and Warren[12]; it is 2.25×10^{-2} cm³/mole of atoms. The enthalpy change at the critical temperature measured by Schkolnick and Quimby[13] is 277 cal/mole. Using these values, $dT/dP = 1.3$°K/kbar. The curve in Fig. 5 is drawn to have this initial slope.

THE KINETICS OF ORDERING

The kinetics of the ordering reaction below T_c were studied in samples annealed for 90 h at 368°C so as to attain an antiphase domain size of about 100 lattice spacings. These samples were quenched and then held
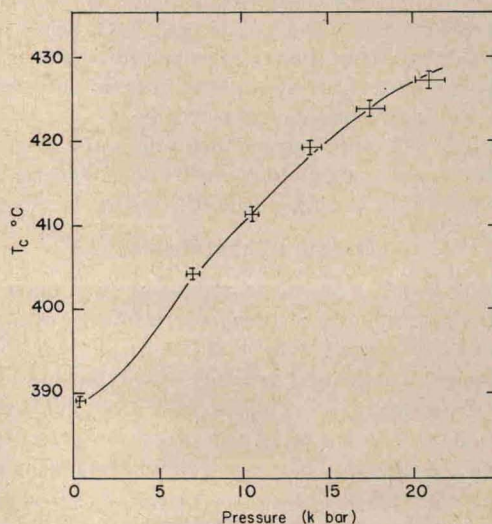

FIG. 5. Observed dependence of the critical temperature for ordering on the pressure.

[11] R. E. Hanneman and H. M. Strong, ASME Publication 61-WA/PT-21 (1964).

[12] D. T. Keating and B. E. Warren, J. Appl. Phys. **22**, 286 (1951).

[13] L. J. Schkolnick and S. L. Quimby, *The Temperature Variation of the Order Dependent Configurational Energy and the Latent Heat of the Order-Disorder Transformation in* Cu₃Au (Thesis by L. J. Schkolnick, Columbia University, 1962).