Melting of Copper, Silver, and Gold at High Pressures*

LEWIS H. COHEN
College of Engineering, University of California, Berkeley, California
AND
WILLIAM KLEMENT, JR.
Department of Physics, University of California, Berkeley, California
AND
GEORGE C. KENNEDY
Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California

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The melting points of copper, silver, and gold have been determined up to about 40 kbar by means of differential thermal analysis in piston-cylinder apparatus. The melting curve of gold shows definite curvature in the explored pressure range, and slight curvature is suggested for copper; the melting temperature of silver rises linearly with pressure. The experimentally determined initial slopes, without any corrections attempted for the effects of pressure on thermocouple emf, are (in °/kbar): Cu, $\sim 3.9_5$; Ag, 5.87 ± 0.27; Au, $\sim 6.1_2$. Previous results of Gonikberg, Shakhovskoi, and Butuzov for copper, of Kennedy and Newton for silver and of Decker and Vanfleet for gold agree inadequately with the present data. Comparison of initial melting slopes with those predicted from thermodynamic data allows evaluation of proposed pressure corrections to emf of Pt versus Pt+10%Rh thermocouples; those proposed by Hanneman and Strong are shown to be too large. The linearity of the melting curve of silver, combined with its ease of containment, suggests its use for high-pressure, high-temperature calibration. Bounds for the initial variations in the volume changes of fusion with pressure may be estimated from the present results and zero-pressure data. The Lindemann relation for melting is examined for copper, silver, and gold by comparing the present results for melting with the 300°K data for the elastic moduli and their variation with pressure; agreement does not appear to be adequate.

INTRODUCTION

COPPER, silver, and gold comprise a group of metallic elements with well-investigated physical, chemical, and structural similarities. As with many other groups of related elements,[1] investigation at high pressures should serve to elucidate many of the similarities and differences in better detail. Some of the most important data which are unique to high-pressure experimentation are determinations of the trajectories of phase boundaries. Since copper, silver, and gold crystallize, insofar as is known, only in the face-centered cubic structure, the study of phase relations reduces to a determination of the melting curves. One report each for the melting of copper,[2] silver,[3] and gold[4] at high pressures exists in the literature; the present experiments were undertaken to test and extend these data, if possible, and to compare them with the predictions calculated from zero-pressure data. From an experimental and engineering viewpoint, precise and accurate determination of such phase transitions would be extremely useful in the calibration of many types of high-pressure apparatus at high temperatures. From a more fundamental point of view, the data for melting can be usefully compared with similar data for other series of elements and with theory in the search for generalizations.

GENERAL EXPERIMENTAL PROCEDURES

Quasi-hydrostatic pressure was generated in piston-cylinder apparatus, with the furnace assembly similar to the design described elsewhere[5] except that fired boron nitride was used instead of talc inside the carbon heating element. The metallic capsules employed to contain samples in the copper and silver experiments were sealed with stoppers of Pyrex, which softened at the operating temperatures and prevented escape of the liquid. For experiments with the more reactive gold, the capsule was almost entirely Pyrex. Transitions were detected by differential thermal analysis[6] using Pt versus Pt+10% Rh thermocouples. At a given pressure, the melting and freezing signals were reproducibly observed at leas three times, with a typical precision and reproducibility of $\pm 1°$, before the datum point was considered as determined. The signal on heating, at a given pressure, was taken as the equilibrium temperature for the transition. Often on decompression, the initial heating signal was observed to lie higher in temperature than the subsequent, reproducible signals, this effect probably being due to relaxation of friction in the apparatus. As discussed elsewhere,[6] the initial datum in a given run is taken only at pressures above 10 kbar or so because of mechanical limitations. The

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