much wider composition range than in any of the other systems. Measurements were made from sulfur-rich Ag_2S to almost pure silver, and Fig. 4 shows that around stoichiometry the conductivity was fairly low, 200 ohm^{-1} cm^{-1}, and was almost independent of composition. However, as the immiscibility region was approached, the conduction of the single liquid phase developed a marked composition dependence, which continued all the way to almost pure silver. Fig. 7 shows details of the region around the composition Ag_2S. On the sulfur-rich side of stoichiometry, readings were very difficult to obtain because of the high sulfur pressure, but there might be a slight upward slope. On the silver-rich side, as in the copper system, there also seemed to be a very slight composition dependence until very close to the boundary of the immiscibility region at about 30 at. pct S at 1000°C. At compositions slightly on the sulfur-rich side of this boundary, the conductivity increased rapidly with increases in the silver content of the melt. Across the almost horizontal portion of the plot, the temperature coefficient was small and positive, but when the region of sudden increase in conductivity was reached, the temperature coefficient became immeasurably small and remained thus until, at about 15 at. pct S, it became definitely negative. This negative dependence on temperature became progressively larger as the silver content increased.

The conductivity of the solid Ag-S system, around the composition Ag-S, has been investigated by a number of workers, and the available data are summarized by Hebb.[7] Essentially, the high temperature, α, form exhibits predominantly electronic conductivity of between 30 and 70 ohm^{-1} cm^{-1}, with the conductance of the sulfur-rich material showing a positive temperature coefficient and that of the metal-rich material a negative temperature coefficient at temperatures between 177° and 500°C. The conductivity of molten Ag_2S has been investigated by Velikanov[8] and was found to fit the equation $\log \sigma = 1.6245 + 553.72/T$. This equation gives values in rough agreement with the data obtained in the present investigation, but, of course, the temperature coefficient carries the opposite sign. No explanation can be offered for this.

It should be mentioned that it is unlikely that any of the measurements reported above for any of the systems studied were inadvertently taken at temperatures below the melting points or other phase boundaries. Accidental passage through a phase boundary, if it did not cause the silica sheaths to break, was always detectable because of a very definite and sudden change in the conductivity, and such readings have not been included in the results quoted in this paper.

DISCUSSION

The copper and silver systems will be discussed first, and in each case it will be assumed that the molten material would behave as an intrinsic semiconductor at the stoichiometric composition M_2S. Practical and statistical considerations at these elevated temperatures make it extremely unlikely that any measurements were made with the melt precisely at the stoichiometric composition. No attempt will be made to speculate whether electron or hole conduction is predominant, since only the relative mobilities of electrons and holes are involved, and these are immaterial to the present discussion.

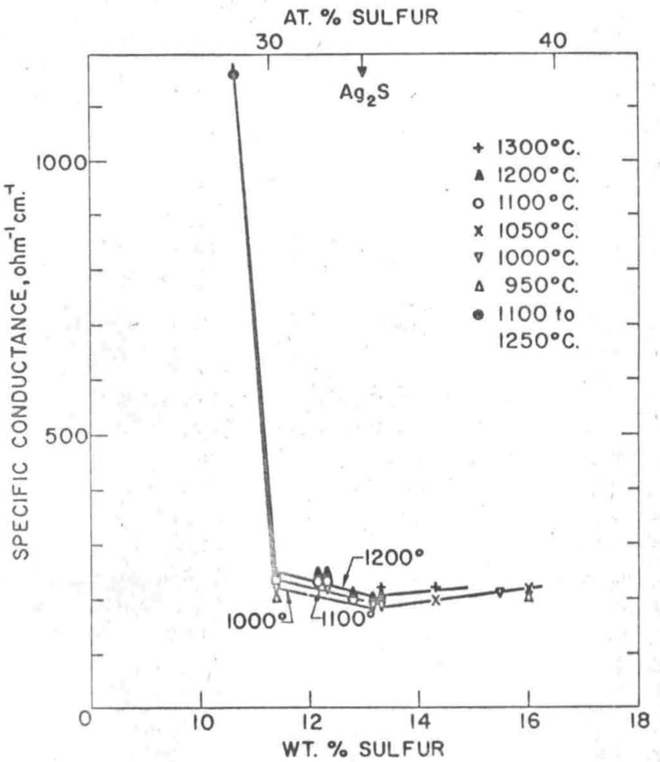

Fig. 7—Details of specific conductance vs sulfur content in the region of the stoichiometric composition Ag_2S.

As metal is added to the stoichiometric material, assuming that excess metal atoms act as donor impurities, some of the electrons from the ionized donors go into the conduction band and the others progressively reduce the number of holes in the valence band. Meanwhile, as more donor atoms are added, the Fermi level rises, and at a composition only slightly on the metal-rich side of stoichiometry, the concentration of free electrons becomes sufficiently large, at 1100°C, 3×10^{19} cm^{-3}, for degeneracy to begin to appear.[9] From this composition onwards, the addition of more metal causes the Fermi level to rise in the conduction band. The number of conducting electrons increases and the number of holes decreases. The very nearly constant conductivity over a considerable composition range, in both the Ag-S and Cu-S systems, bears out this postulation, *i.e.*, electron conduction is increasing while hole conduction is decreasing. The approximately constant value of the positive temperature coefficient across the same range is also consistent, since it implies that the energy of the gap is large compared with the distance the Fermi level moves in the conduction band.