

# Electrical Conductivity of the Molten Co-S, Ni-S, Cu-S, and Ag-S Systems

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*nickel sulfide  
electrical conductivity  
diamond*

*The electrical conductivities of Co-S, Ni-S, Cu-S, and Ag-S melts were studied as functions of temperature and composition. The specific conductances of the Co-S and Ni-S systems were high, 3500 to 5500  $\text{ohm}^{-1} \text{cm}^{-1}$  and 4500 to 5500  $\text{ohm}^{-1} \text{cm}^{-1}$ , respectively, with minima near the stoichiometric compositions  $\text{Co}_4\text{S}_3$  and  $\text{Ni}_3\text{S}_2$ . Temperature dependence was small and negative. The specific conductances of melts with compositions approximating  $\text{Cu}_2\text{S}$  and  $\text{Ag}_2\text{S}$  were lower, 60  $\text{ohm}^{-1} \text{cm}^{-1}$  and 200  $\text{ohm}^{-1} \text{cm}^{-1}$ , respectively, with very small, positive temperature coefficients, and, close to stoichiometry on the metal-rich side, negligible composition dependence. Immediately on the sulfur-rich side of  $\text{Cu}_2\text{S}$  the conductivity rose rapidly, but no similar change was observed in the Ag-S system. It was possible to measure the conductivity of the single liquid phase over the whole composition range  $\text{Ag}_2\text{S}$  to pure silver. A rapid increase in conductance, beginning at about 30 at. pct S and continuing to pure silver, was observed. It was accompanied by a change to a negative temperature dependence. A qualitative energy-level model is proposed in which the systems are treated as degenerate semiconductors over most of their composition ranges.*

RECENT measurements of the electrical conductivity of the molten Cu-S and Fe-S systems<sup>1-4</sup> indicated that the conduction was electronic, and this has been interpreted by means of energy-level diagrams of the type used for solids. The present investigation is part of a series in which an attempt is being made to obtain an overall picture of electrical conduction in liquid systems of this kind, and with this end in mind, the specific conductance of molten Co-S, Ni-S, and Ag-S has been measured over as large a range of temperatures and compositions as was found to be practicable, and a few additional measurements were also made in the Cu-S system.

## EXPERIMENTAL

**Materials.** The sulfur compounds were prepared from the elements (reagent grade) by heating together the appropriate proportions in vacuum or in

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an atmosphere of argon. Care is needed in the preparation of the Co-S and Ni-S compounds since, once the reaction starts, at 200° to 400°C, it is violently exothermic.

In the course of a series of measurements, the sulfur content of the melt could be increased at will by passing  $\text{H}_2\text{S}$  through or over the melt; it could be decreased by passing argon, or by dropping pellets of metal into the melt.

Samples were removed from the Co-S, Ni-S, and Cu-S melts by sucking some of the material up into 3 mm quartz tubing. The whole sample was analyzed because of a tendency to segregate. This sampling technique was not entirely satisfactory with Ag-S melts of some compositions (particularly 4 to 11 wt pct) because of separation into two liquids as the material cooled, with loss of some of the dense liquid from the bottom of the sampling tube. This difficulty was overcome by using a silica ladle. The samples were analyzed for the metals, and sometimes for sulfur also, by standard techniques. At high sulfur contents, samples were taken before and after conductivity measurements because of possible loss of sulfur during the readings, but at lower sulfur contents, samples were taken only once, either before or after measurements.

**Apparatus.** The melt was contained in a straight-side,  $\Delta$  RR Morganite, recrystallized alumina crucible supported on a small inverted crucible in the bottom of a closed-end mullite tube. Heating was accomplished by means of a Globar furnace, and the temperature was measured by a Pt-Pt/Rh (10 pct) thermocouple which was protected by a McDanel sheath which dipped into the melt at the time of measurement. Auxiliary equipment allowed the passage of pure, dry argon or dry  $\text{H}_2\text{S}$  as required.

**Conductivity Cell.** The conductivity was measured using a four terminal cell<sup>1-4</sup> and a dc potentiometer circuit. The cell, with two current carrying electrodes and two null current probes, all of graphite, and enclosed in double-bore clear silica sheathes with a short, single bore capillary at the lower end, was essentially the same as that used in previous work.<sup>4</sup> However, a slight modification was incorporated so that argon or  $\text{H}_2\text{S}$  could be blown via sidearms through the electrode sheathes between measurements in order to get fresh material from the bulk of the melt into the capillaries for each conductance measurement. The electrode sheathes were held at the upper ends in a rubber stopper together with the thermocouple and a gas outlet tube. This rubber stopper fitted into a glass

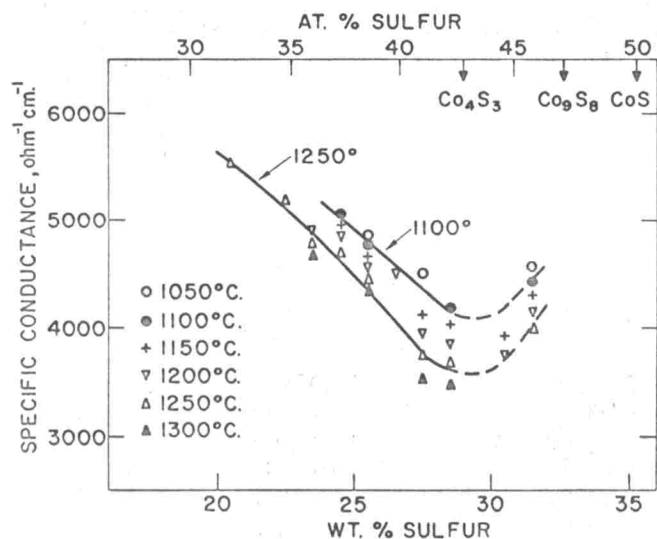


Fig. 1—Specific conductance vs sulfur content for Co-S.

tube, about 9 in. long and with a gas inlet sidearm, and which passed through a large rubber stopper fitted into the top of the McDanel reaction jacket, which was cooled by a fan. When the glass tube was lubricated with silicone grease, it slid readily through the large stopper, enabling the cell to be lowered into or raised from the melt at will.

**Measurements.** Before use, the conductance cells, which usually had a cell constant of about  $15 \text{ cm}^{-1}$ , were calibrated using mercury at room temperature. In this calibration, and in the measurements on the melts, direct current of about 5 amp from a lead storage battery was used, and the potential drop across the cell was compared with the potential drop across a standard 0.001 ohm resistor, using a Leeds and Northrup K2 potentiometer.

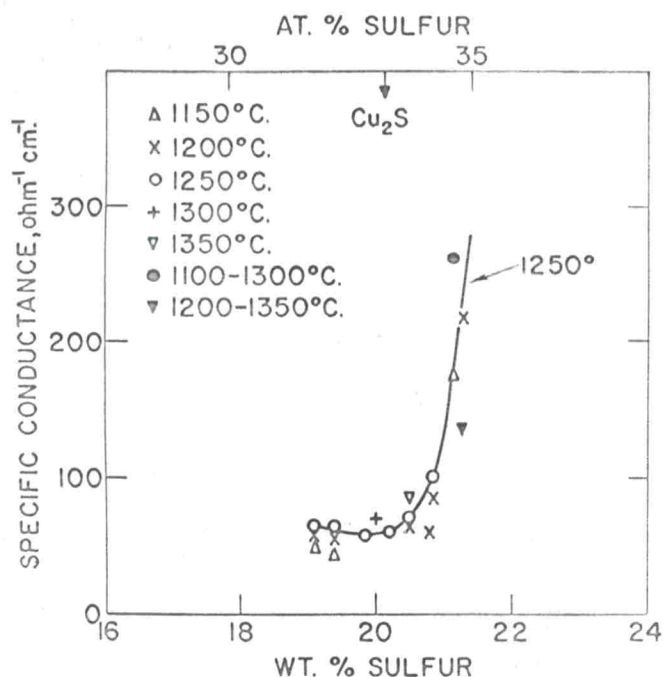


Fig. 3—Specific conductance vs sulfur content for Cu-S.

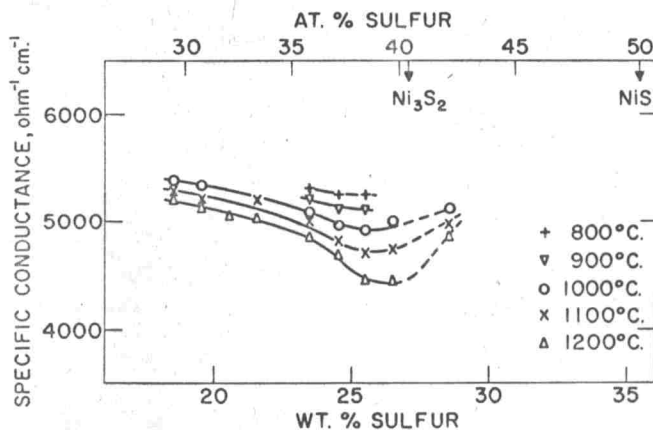


Fig. 2—Specific conductance vs sulfur content for Ni-S.

When taking measurements on the melts, the potential drop was measured, the polarity was reversed, the measurements were repeated, and an average value of the two readings was used to calculate the conductivity. This technique eliminated errors caused by thermal electromotive forces produced at the junctions of the graphite electrodes and the molybdenum leads. Although these junctions were constructed identically, and were in the same temperature zone, it was found, in practice, that considerable error could be introduced if readings were taken with the current passing in one direction only.

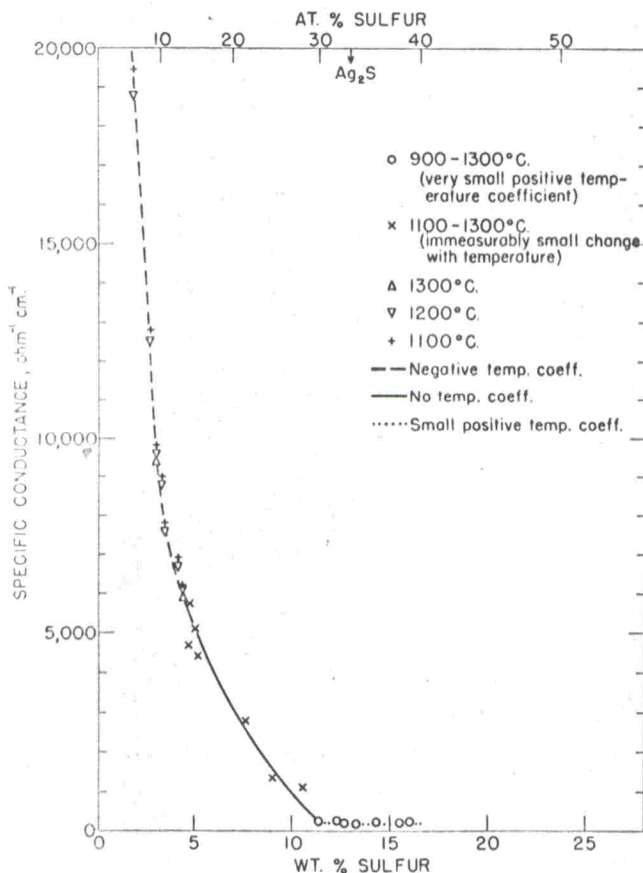


Fig. 4—Specific conductance vs sulfur content for Ag-S.