

Eventually, a metal-rich composition is reached at which the Fermi level is sufficiently high in the conduction band for there to be no further excitation of electrons from the valence band, and hence no further production of holes. Thenceforth, the conductivity is metallic in nature. It would be expected that the conductivity would begin to rise rapidly, and would continue to do so all the way to the pure metal, and that the positive temperature coefficient would disappear and be replaced by a negative one. These changes were observed in the Ag-S system. Phase diagram difficulties precluded similar observations on the Cu-S system, but there is no reason to doubt that it would behave similarly.

A similar explanation can probably be offered for the sulfur-rich side, with sulfur acting as an acceptor impurity close to stoichiometry, and the Fermi level moving down until it is in the valence band, when the system becomes degenerate. At some more sulfur-rich composition a rapid increase in conductivity would be expected; this was observed in the Cu-S system but not in the Ag-S system, even at the most sulfur-rich composition that could be studied. Of course, the distance from stoichiometry at which the discontinuous rise in conductivity occurs depends on the shape of the bands and will be specific to each case. It is hoped that current measurements on Cu-Te and Ag-Te melts will clarify the behavior on the metalloid-rich side of stoichiometry.

The suggestions made in the above paragraphs will be discussed rigorously by W. R. Bitler¹⁰ in a forthcoming paper.

Considering next the Co-S and Ni-S systems, it will be assumed, as with Fe-S,⁴ that the stoichiometric compounds, Co₃S₂ and Ni₃S₂, are intrinsic semiconductors where the forbidden gap between valence band and conduction band is small. This assumption is supported by the high conductivities and small negative temperature dependence; the latter would indicate that thermal promotion of electrons is more than offset by loss of mobility of the conducting species through thermal scattering. The minima in specific conductance in the region of stoichiometry can be explained qualitatively using the model proposed for the Cu-S and Ag-S systems. However, a rigorous examination of the cobalt and nickel systems would probably be difficult because of the complicated band structure of the transition metals.

One fact emerges clearly from the above considerations. In none of the systems studied would it be legitimate to attempt to describe the behavior of the donor or acceptor impurities in the manner of

Baumbach and Wagner.¹¹ These workers were considering only very small deviations from stoichiometry, and hence only low concentrations of carriers, where classical statistics are applicable and

$$n = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\epsilon/kT}$$

In the present investigation and in the work of Argyriades, Derge, and Pound⁴ on the molten Fe-S system, vastly larger composition ranges were covered, and the classical approximation would be inapplicable to all but a minute portion of the range since, for example, at 1100°C this approximation breaks down when the total number of free electrons is greater than $3 \times 10^{19} \text{ cm}^{-3}$. This number would be exceeded when the composition deviated from stoichiometry by less than 0.001 wt pct Ag in the case of Ag₂S, and the system would then begin to become degenerate. Thus the Baumbach and Wagner treatment can be applied only in a very small composition range on either side of the stoichiometric compound, and measurements within such small limits would be virtually impossible with these molten materials.

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