Letters to the Editor.

A Note on the Magnetic Susceptibilities of Cuprous Oxide Films.

WHEN a thin strip of metal is heated by insertion of an edge of it in a bunsen flame, a very thin layer of an oxide film is formed on the metallic surface. The structure of these oxide surfaces has been studied by J. A. Darbyshire[1] and also by W. L. Bragg and J. A. Darbyshire,[2] who have shown by the method of electron diffraction that in the case of copper, the oxide that is formed is of the usual cubic structure of cuprite, Cu_2O. As the composition of the film is a controversial question and the literature describes the film to consist of a mixture of Cu_2O and CuO, it has been considered desirable to examine the question from a magneto-chemical point of view.

The cuprous oxide in the powdered state, when pure and not contaminated with CuO, has been found to be diamagnetic with a value of χ equal to $-0{\cdot}188\times10^{-6}$ as determined by the Bhatnagar-Mathur Magnetic Interference Balance. The literature on the subject of the magnetic properties of Cu_2O is highly controversial. For example, the *International Critical Tables*, Vol. VI, page 357, describe the substance to be paramagnetic with a value of $+1{\cdot}2\times10^{-6}$, whilst E. H. Williams[3] describes the cuprous oxide to be diamagnetic. Klemm and Schüth[4] have also recently found that Cu_2O has a value χ equal to $-0{\cdot}18\times10^{-6}$ and is diamagnetic. This value of the susceptibility of cuprous oxide is in good accord with the figure $-0{\cdot}188\times10^{-6}$ obtained by us. Two different samples of Cu_2O, prepared by different methods: (i) by the reduction of alkaline $CuSO_4$ with glucose; and (ii) by the electrolysis of a hot boiling solution of NaCl, between copper electrodes, have been examined by us. In both these cases the Cu_2O was found to be diamagnetic and the values of χ were $-0{\cdot}188\times10^{-6}$.

The next step was to examine the films of oxides on copper. They were prepared firstly by heating a clean piece of copper

[1] J. A. Darbyshire. *Trans. Faraday Soc.*, **27**, 675, 1931.

[2] W. L. Bragg and J. A. Darbyshire. *Trans. Faraday Soc.*, **28**, 522, 1932

[3] E. H. Williams. *Phys. Rev.*, **28**, 167, 1928.

[4] Klemm and Schüth. *Z. anorg. allgerm. Chem.*, **203**, 104, 1931.

foil as described by Darbyshire and secondly by following the method of Sebatier and Senderens which consists in heating the metallic foil in an atmosphere of nitric oxide to a temperature of about 250°C. A very fine film of copper oxide was formed on the metallic surface, in both the cases. These films are supposed to consist of Cu_2O only and no CuO is supposed to be formed. The films so prepared were removed from the surface of copper by the method employed by U. R. Evans[5] and on investigation were found curiously enough to be definitely paramagnetic, as against the Cu_2O in bulk which we showed definitely to be diamagnetic. There are only two explanations of this behaviour. Firstly, that the film is contaminated with a paramagnetic material, possibly the CuO and secondly, that the magnetic properties of the Cu_2O in film are different from those of the substance in bulk. The second view is not possible on account of the fact that Cu_2O was prepared by different methods and consisted of all sizes of particles: The values of χ however in all the cases of different sizes of particles were nearly always equal to $-0{\cdot}188\times10^{-6}$ both in our experiments and in those of Klemm and Schüth. Also in view of the recent work of Lane[6] that the particle size of the film of bismuth has no effect on its susceptibility and that the films examined are paramagnetic, it looks likely that the impurity responsible for the paramagnetism of these films is the production of a trace of the paramagnetic CuO. Further support in favour of this view comes from a recent entirely different investigation of G. Athanasiu,[7] who, in course of his investigations on the spectral sensitivity of photovoltaic piles of copper electrodes coated with Cu_2O, has shown that the presence of a trace of CuO in the sub-oxide tends to diminish the E.M.F. produced by light and also displaces the maximum of sensitivity towards the red end of the spectrum. He coated the plates of copper with thin films of Cu_2O by three different methods and the effects obtained by him are in some cases positive and in others negative, depending on the presence or absence of CuO, as a contamination in the Cu_2O films. According to this author, the films prepared by heating copper in electric furnace contain a good amount of CuO. When these black scales of CuO are removed the positive effect noted above on the photo-galvanic effect of Cu_2O is totally suppressed.

From the magneto-chemical data and the work of Athanasiu it appears probable that the Cu_2O films prepared in the manner described in this paper, contrary to the evidence obtained by Bragg and Darbyshire, consist of a mixture of both Cu_2O and CuO. A fuller account of the work will be presented elsewhere.

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[5] U. R. Evans. *Jour. Chem. Soc.*, 2651, 1929.
[6] C. T. Lane. *Nature*, December 31st, 1932.
[7] G. Athanasiu. *Comptes Rendus*, **195**, 767, 1932.