faces. This may be seen by comparing Fig. 1a with Fig. 1b, which is a photograph of a 'Perspex' dodecahedron with spheres at the centres of each face.

The crystal photographed was about 315μ across and the inclusions were about 20μ across. The regularity of their pattern suggests that the mechanism of their formation is closely linked to the crystal symmetry and work is in progress to elucidate this mechanism.

K. G. DENBIGH
E. T. WHITE

Imperial College of Science and Technology,
Department of Chemical Engineering and Chemical
Technology,
Prince Consort Road,
South Kensington,
London, S.W.7.

[1] Denbigh, K. G., *Farad. Soc. Disc.*, No. 5, 188 (1949).

METALLURGY

Electrochemical Properties at the Curie Point

SOME preliminary work with gadolinium (Johnson, Matthey and Co., Ltd.: Curie point, 16° C) has shown that this metal exhibits maximum electropositivity in the curie point region (Fig. 1).

The apparatus used consisted of an H-cell and each limb was connected by a closed and ungreased tap. The limbs and connexion were filled with the appropriate electrolyte. Each limb was provided with a similar electrode, thermometer and temperature control, one limb (the reference electrode) being kept at 21° C. The H-cell e.m.f. was measured directly with a 'Vibron' electrometer.

The selection of electrolyte, and preparation and ageing of electrodes, were governed by the requirement that a reproducible and steady cell e.m.f. should be quickly attained under standard conditions. It is emphasized that, in this type of comparative work, steady-state potentials (whether mixed or not) can be used without recourse to fulfilling stringent thermodynamic requirements for the sake of obtaining equilibrium or standard electrode potentials[1]. When a temperature difference exists between the two limbs, or half-cells, then it can be shown that the plot of H-cell e.m.f. versus temperature should be smooth. This smooth or normal behaviour was exhibited only by the copper, zinc and Monel electrodes.

Thus the electrolyte used for gadolinium was N potassium chloride + hydrochloric acid (pH 5) and a small amount of hydrogen evolution occurred in both half-cells.
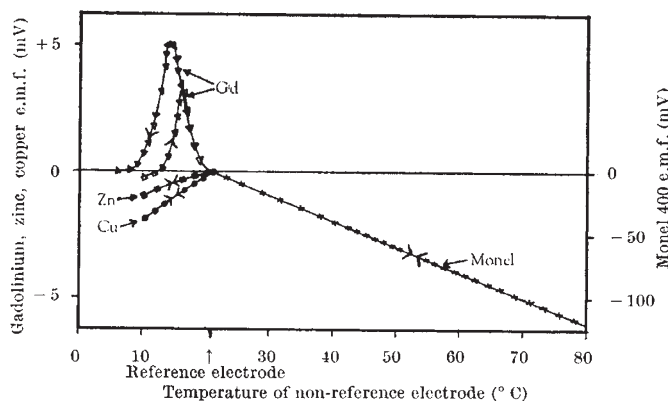

Fig. 1. Graph showing plot of H-cell e.m.f. versus temperature of non-reference half-cell for various metal-electrolyte systems. The sign of the e.m.f. is that of the non-reference electrode and, for the purpose of clarity, the plots have been confined to temperatures: (a) below 21° C for gadolinium, zinc and copper and (b) above 21° C for Monel 400

Fig. 1 also shows the results obtained using: (a) zinc, in N potassium chloride + hydrochloric acid (pH 5)—a system similar to gadolinium since very slow hydrogen evolution occurred; (b) copper, in N copper sulphate + N sulphuric acid—a system where no hydrogen evolution occurred; (c) Monel 400 (Henry Wiggin and Co., Ltd.) in N potassium chloride + hydrochloric acid (pH 1)—this alloy possesses a Curie point in the range 45°–60° C, but no 'gadolinium effect' was observed.

The gadolinium effect suggests that the rearrangement of $4f$ electron energy-levels at the onset of ferromagnetism affects also the valency electrons. The factors contributing to the e.m.f. of the type of cell used in these experiments which are affected by the ferromagnetism of one electrode are the work function φ and sublimation energy S (ref. 2). Changes in these quantities $\Delta\varphi_f$ and ΔS_f due solely to ferromagnetism can be estimated in the case of a copper–nickel alloy such as Monel, in which there is overlap between the nearly filled $3d$ band and the $4s$ band, on the basis of the collective electron theory of ferromagnetism[3,4].

The dominant term is $-\dfrac{1}{9}\int_0\sigma^2$ in $\Delta\varphi_f$ where σ is the temperature-dependent relative spontaneous magnetization and $\int_0$ the common Fermi energy of $3d$ and $4s$ electrons below the top of the $3d$ band at absolute zero (where ferromagnetism is absent). Using Wohlfarth's data[4] the net effect on the cell e.m.f. can be estimated to be for Monel $0.011 \, (1 - T^2/\theta^2)$ V, where T is the absolute temperature and θ the Curie temperature, and in such a sense as to make the ferromagnetic electrode more electropositive. This effect is so small in Monel (due to a small $\int_0$) that no change in slope at θ is evident in the e.m.f. versus temperature graph.

The gadolinium effect, though complicated by hysteresis and possibly by a short-range order effect above θ, could perhaps be explained by a similar approach if more were known of the density of states function of the half-filled $4f$ band and the extent of overlap with the valency electron bands. However, in order to establish any mechanisms, further work is clearly necessary, but it is believed that the electrochemical approach may be useful in exploring the difficult subject of ferromagnetism.

J. K. PRALL
P. R. DOIDGE

Battersea College of Technology,
Battersea Park Road,
London, S.W.11.

[1] Kortum, G., and Bockris, J. O'M., *Textbook of Electrochemistry*, 1, 228 (Elsevier, London, 1951).
[2] Kortum, G., and Bockris, J. O'M., *Textbook of Electrochemistry*, 1, 255 (Elsevier, London, 1951).
[3] Stoner, E. C., *Proc. Roy. Soc.*, A, 169, 339 (1939).
[4] Wohlfarth, E. P., *Proc. Roy. Soc.*, A, 195, 434 (1949).
[5] Stoner, E. C., *Proc. Roy. Soc.*, A, 165, 372 (1938).

Epitaxial Oxide Growth on Thin Single-crystal Gold – Nickel Alloy Films

THE oxidation characteristics of binary alloys and the growth and structure of oxidation products on such alloys have been examined by various investigators[1-3]. However, the only published evidence on the oriented growth of such oxidation products is that of Honjo[2]. He has reported on selective oxidation of beryllium in a beryllium-copper alloy and observed that the BeO phase grows with a preferred orientation in which the [00,1] axis is perpendicular to the free surface of the specimen. The origins of this orientation were not explained. This communication describes a novel orientation effect observed in the oxidation of thin epitaxed films of a noble metal alloy containing a small percentage of an easily oxidizable transition metal. The alloy examined was a gold–nickel alloy containing 5 wt. per cent of nickel. The growth and structure of the alloy and its oxide were investigated by transmission and reflexion electron diffraction techniques.