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p-Bromobenzoic anhydride and biferrocenyl – corrigenda.

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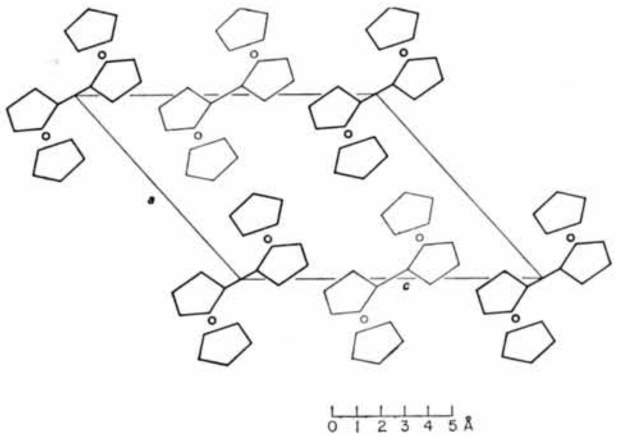

Biferrocenyl: corrected Fig. 3.

In the paper on *p*-bromobenzoic anhydride (McCammon & Trotter, 1964) x of C(7) should be 0·116. In that on biferrocenyl (Macdonald & Trotter, 1964) Fig. 3 is incorrect; the correct version is shown.

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On the existence of hexagonal nickel.

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In text books on X-ray diffraction (*e.g.* Cullity, 1956; or Glocker, 1958) nickel is listed as crystallizing in the h.c.p. (*A*3) modification, in addition to the f.c.c. (*A*1) structure. The hexagonal lattice parameters reported there as $a=2{\cdot}66$ Å, $c/a=1{\cdot}624$ and $a=2{\cdot}66$ Å, $c/a=1{\cdot}61$, respectively, are given without special references and apparently originated in older and somewhat doubtful sources. [For a brief survey of the situation see Pearson (1958, p. 780)]. In some cases, the presumptive hexagonal phase has been shown to be instead Ni_3N (Büssem & Gross, 1934; Jack, 1950). From these results, it may be concluded that pure nickel does not form a hexagonal phase, but that the hexagonal structures reported were due to the formation of hydrides, nitrides, and possibly carbides or carbonitrides (Pearson, 1958, p. 780). Even so, the question as to exactly whether or not hexagonal nickel does in fact exist, appears to be still not completely settled (Heavens, 1959).

The purpose of this note is to show that in thin (about 200 Å thick) nickel films, when evaporated at about 10^{-5} torr, the hexagonal close-packed structure can be produced under certain circumstances.

During high magnification viewing in the electron microscope of nickel and nickel-rich Ni–Cu films, prepared for magnetic structure investigations (Hemenger, 1964; Weik & Hemenger, 1965), some nickel films exhibited what appeared to be a rapid grain growth. The grain size of these large particles varied between 500 and 1200 Å, as compared to a grain size for normal films of 50 to 125 Å.

Fig. 1 shows an electron diffraction pattern, which was taken of the film region containing the large grains within the matrix of the normal grains of the film. The continuous rings are due to the normal, f.c.c. nickel and are indexed, while the spotted rings are due to a new structure, which is obviously associated with the large grains.

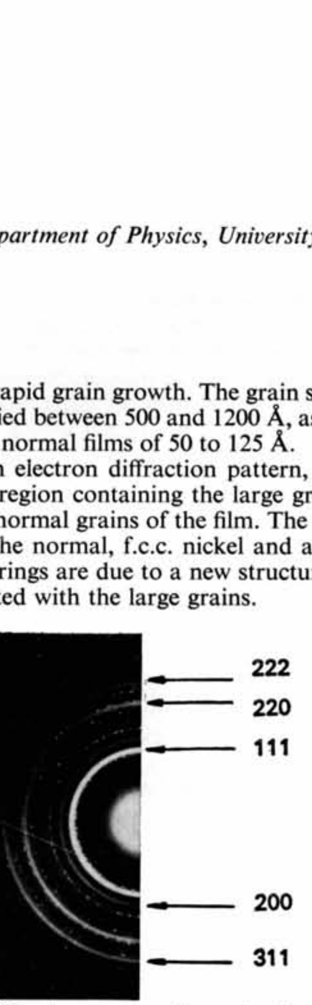

Fig. 1. Electron diffraction pattern of a region in a nickel film containing large grains within the normal fine grain matrix. The continuous rings are due to the normal f.c.c. nickel matrix and are indexed.

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Using the f.c.c. nickel lines as an internal standard, the spotted rings could be indexed as the reflections of a h.c.p. structure with

$$a=2{\cdot}622\,,\quad c=4{\cdot}320\ \text{Å};\quad c/a=1{\cdot}648. \tag{1}$$

In Table 1, the measured d values of the spotted reflections are listed together with d values calculated with the use of the relation

$$d=\frac{a}{\sqrt{\frac{4}{3}\,(h^2+hk+k^2)+(a/c)^2l^2}} \tag{2}$$

with the above a and c parameters, and, for comparison, with d values for the hexagonal Ni_3N. Note that all observed spotted reflections could be indexed with extremely good agreement between observed and calculated lines, while the agreement between the measured d values and those of Ni_3N is only fair; note especially the Ni_3N value 1·155 Å and the missing 1·098 Å value. In addition to the lack of d-value agreement, the a and c values are also different. Jack (1950) gives for Ni_3N

$$a=2{\cdot}667\,,\quad c=4{\cdot}3122\ \text{Å};\quad i.e.\ c/a=1{\cdot}617\,,$$

which are quite noticeably different from the values found above. NiO, on the other hand, which might have formed during evaporation in the relatively poor vacuum, crystallizes at room temperature in the rhombehedral structure (Pearson, 1958, p. 1021), which, after transformation to the equivalent hexagonal description, yields $a=2{\cdot}955$, $c=4{\cdot}207$ Å, and thus a much smaller c/a ratio than the structure found in the investigated nickel films. Therefore, the evidence is very strong that the observed structure is in fact a hexagonal phase of nickel.

The grain growth was observed only when a high-intensity electron beam was used; furthermore, the effect was observed near tears in the films, which then were curling during viewing. Therefore, it is believed that the transformation of f.c.c. nickel to the hexagonal form is due to a combination of heating and straining. A more detailed presentation of the proposed mechanism will be given elsewhere.

Note added in proof: In a recent article, Wright & Goddard (1965) reported that nickel may be electro-deposited to form a single-crystal hexagonal structure, provided that correct bath conditions and suitable substrates are used. The lattice parameters were determined as $a=2{\cdot}50\pm0{\cdot}01$ Å; $c/a=1{\cdot}59\pm0{\cdot}01$. It was observed that – in agreement with our own observations – the growth conditions are extremely critical for the formation of the h.c.p. structure, which was found to be unstable at room temperature.

Table 1. *Measured and calculated d values*

Expected hexagonal lines	Measured d values of the spotted rings	Calculated d calues using equations (1) and (2)	d values for Ni_3N from ASTM card No. 10–280
($hk\cdot l$)	(Å)	(Å)	(Å)
(10·0)	2·27	2·271	2·311
(00·2)	2·159	2·160	2·144
(10·1)	Superimposed on Ni ring (111)	2·010	2·035
(10·2)	1·565	1·564	1·576
(11·0)	1·311	1·311	1·333
(10·3)	1·216	1·218	1·219
			1·155
(20·0)	1·135	1·135	1·133
(11·2)	1·119	1·120	1·115
(20·1)	1·098	1·098	
(00·4)	1·081	1·080	1·076
(20·2)	Superimposed on Ni ring (222)	1·005	1·018

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A knowledge availability survey of the crystal structural data for pyrimidine derivatives.

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Many of the biologically interesting molecules involved in life processes contain the pyrimidine ring. Consequently, up to February 1965, about one hundred twenty single-crystal structure determinations by X-rays or neutrons have been reported in more or less detail on compounds containing the pyrimidine ring, *i.e.* pyrimidines, barbiturates, purines, nucleosides, nucleotides, *etc.*

The crystal structural information obtained from these investigations (*i.e.* crystal data, valence and hydrogen bond lengths, angles, *etc.*) has been punched on cards in a format suitable for a uniform representation as well as for information retrieval by means of a card-sorting machine or a computer. These structural data, together with the explanatory report, are available to crystallographers at nominal mailing charges. Inquiries should be addressed to The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh, Pa. The data are available in the following choice of format: