lattice parameters and crystal structures, since the latter has a defect spinel structure, reflexions forbidden by the true spinel lattice will occur. Of these the {011} should be approximately 4/9 as intense as the {220} according to the *X-ray Powder Diffraction File* of the American Society for Testing and Materials[3]. Fig. 2 shows no evidence of this.

The oxide pattern comes from more than one crystallographic zone, namely [$\bar{6}11$] and [$\bar{4}11$]. The zone axis of this is thus some 15° from the [100] zone observed by Fursey[1], and this pattern shows four of the {311} reflexions observed by her. The other four {311} reflexions are observed when the zone axis is tilted further away from the [100] so that the [$\bar{2}11$] zone diffracts. Diffraction patterns are most commonly obtained from a range defined by the zone axes [$\bar{6}11$] and [$\bar{2}11$] (ref. 4).

It is likely that this oxide forms by atmospheric oxidation, the shortest exposure to air being sufficient to produce small areas. The diffuse spot patterns from it, the invisibility of it and its appearance on the overheated foil, suggest that it forms initially as a thin layer or as small disk-shaped particles, and that it will preferentially precipitate on ferrite grains which have a cube edge almost normal to the foil surface. The orientation relationship with the matrix will be published elsewhere[4]. It is reasonable to assume that the niobium steel already had a surface oxide layer before overheating in the microscope and that the effect of the heat was to cause growth of the oxide to give the discrete particles shown in Fig. 2.

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Anodic Photocurrent and the Primary Process in Electrochemical Photoeffect

ANODIC photocurrents are often produced when polarized metallic electrodes covered with oxide or other semiconducting material are illuminated in solutions[1]. The primary process is here the generation of a pair electron-hole, which results from the absorption of a light quantum in the surface layer.

A different kind of anodic photocurrent has been found in the case of a dropping mercury electrode illuminated by light not absorbed in the solution. This was observed in solutions of glyoxal, diacetyl, sodium oxalate, dimethyl oxalate, oxalic acid, pyruvic acid, glycine, Cl-acetic acid and a series of α-hydroxy acids. The condition of activity is apparently the presence of a $\diagdown$C=O group in the molecule with a negative substituent on the neighbouring carbon atom. In solutions of compounds giving polarographic anodic currents due to formation of complexes with mercury, such as ethylenediamine tetraacetic acid or ethylenediamine, the anodic photocurrent does not appear.

In a similar fashion to cathodic photocurrents on the dropping mercury electrode[2,3], anodic photocurrents are directly proportional to the surface of the electrode and to the intensity of light; the relation between the energy of the red limit of photocurrent and the potential of the electrode is linear (Fig. 1). However, unlike their effect on cathodic photocurrents, aqueous and ethanolic solutions yield anodic photocurrents of the same order of magnitude.

Since the absorption of light in the bulk of the solution has been excluded in the present experiments and since the absorption by the metallic surface should lead to cathodic photoemission of electrons, there is only one
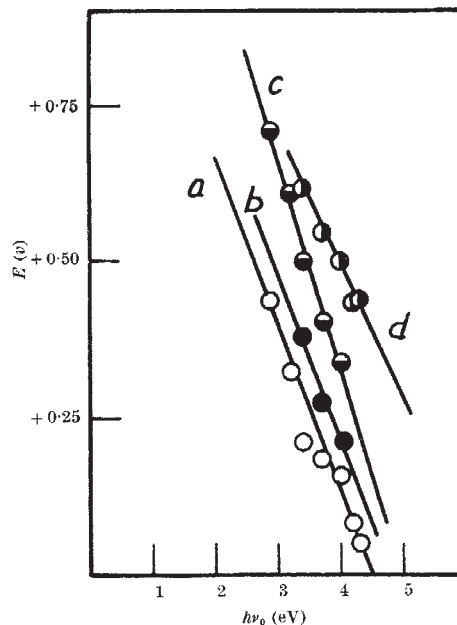

Fig. 1. Relation between the energy of red limit of photocurrent and the electrode potential in: (*a*) 0·1 M sodium tartrate in water; (*b*) 0·1 M oxalic acid in ethanol; (*c*) 1 M oxalic acid in water; (*d*) 0·1 M glycine in water. Potentials measured from the potential of zero charge

possible explanation—that the light-absorbing species responsible for the anodic photocurrent is a complex between the adsorbed organic compound and the surface of the electrode.

The mechanism of photoexcitation of such a complex can be interpreted in terms of the charge-transfer–no-bond theory applied to adsorption[4]. The electrode plays the part of an electron acceptor, the organic molecules are electron donors, and the adsorption bond corresponds to the ground state of the complex. On absorption of light quantum the electron is transferred from the adsorbed substance to the electrode. If the electron returns to the ground state, no direct current can be observed. The occurrence of a photocurrent indicates, therefore, that the complex in its excited state has undergone some secondary irreversible change. In the example given here, this change is probably an electrolytic oxidation of the dative state of the donor.

In solutions of sodium oxalate, for example, judging from the photochemical behaviour of oxalate complexes of mercury[5], it can be assumed that from the oxalate anion in the dative state the oxalate radical-anion $C_2O_4^-$ is formed which, as a strong reducing agent[6,7], is readily oxidized on the electrode to carbon dioxide, thus yielding the anodic current.

The photoexcitation of a charge-transfer complex between the electrode and an adsorbed substance might also explain the primary processes in the cathodic photocurrent in cases where direct emission of electrons is not likely to occur, as it has been observed in aqueous solutions[2,3].

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