tron diffraction, enters exponentially, so if ω_l has, for example, an error of 3 %, the numbers in the fourth column of Table I are uncertain by about 20 %.

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SURFACE STRUCTURES ON THE CLEAN PLATINUM (100) SURFACE

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We have found surface structures to be present on the (100) face of clean platinum single crystals which are different from the substrate structure. One of these structures is stable in the temperature range of $T \approx 350\text{-}550$°C and the other structure in the range $T \approx 750$°C to the melting point (1769°C). We believe that these surface structures are the property of the clean platinum surface. Surface structures which exist on clean semiconductor surfaces have been discovered and studied by Lander and Morrison.[1] No such surface structures, as far as we know, have been found to exist which are attributable only to the atoms of the metal substrate. Nickel[2] shows surface reconstruction only in the presence of gases such as oxygen and hydrogen. Tungsten[3] shows surface structure due to carbon impurities.

We have studied the clean (100) crystal face of platinum of the highest available purity (99.999 %, vacuum electron beam zone refined), using low-energy electron diffraction (Leed by Varian). The crystal, after polishing and etching (with aqua regia), was ion bombarded using ultra-high-purity-grade noble gases (Xe, Ar). After annealing at 250 to 350°C, the crystal surface shows the diffraction pattern characteristic of the regular (100) fcc substrate as shown in Fig. 1(a). After heating the crystal in the temperature range $T \approx 350\text{-}550$°C from 5 min. to 5 h, depending on the temperature, the surface structure, shown in Fig. 1(b), appears. This structure was observed on three different samples in the same temperature range. During heating the ambient pressure remained below 2×10^{-9} Torr. The formation of this structure as measured by its intensity increase is a function of time and temperature. The surface structure slowly disappears at room temperature, but readily reappears when the crystal is reheated to over 400°C (reversible rearrangement). The structure is a property of the surface since its intensity decreases sharply with increasing electron energies.

There are no detectable reflections between the rows of the surface structure pattern [Fig. 1(b)]. Therefore, the existence of a surface net which has the same orientation and five times the lattice parameter (i.e., 5×5 structure) of the substrate net can be excluded. A possible structure which would give rise to the observed pattern shown in Fig. 1(b) is given in Fig. 2. It is a domain structure which is often encountered in perovskite and digenite crystals[4] as determined by x-ray diffraction. One domain shows extra atoms in every fifth row in the x direction, while there is a random arrangement of atoms in the y direction. The other domain is rotated 90°. The observed pattern will be the result of elastic scattering of electrons due to the many domains of perpendicular orientation, as long as the domains are much smaller than the area covered by the electron beam (1mm^2). Observing the pattern as the beam is swept over the crystal supports this conclusion. The domain structure rapidly disappears when the crystal is heated to over 580°C, and the substrate pattern is restored to its full intensity. When the (100) face is heated to a temperature greater than 750°C, a ring structure appears [Figs. 3(a) and 3(b)]. This "disorder" structure shows regular diffraction characteristics. It is concentric about the (00) reflection, has higher order reflections and a wavelength dependence. Once formed, the ring structure is stable in the temperature range 750°C to the melting point (1760°C) until removed by ion bombardment (irreversible rearrangement).

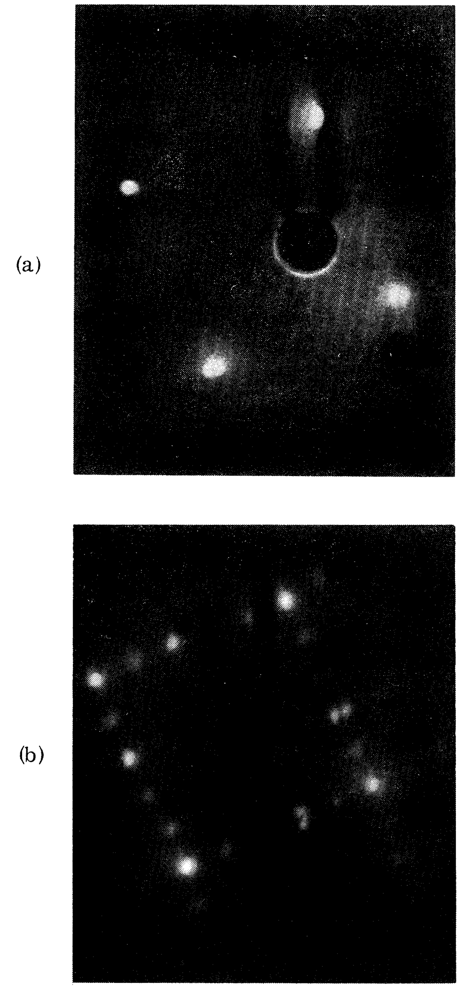

FIG. 1. (a) Diffraction pattern of clean platinum (100) surface at $E = 58.0$ eV. (b) Pattern ($E = 58.0$ eV) of the (100) face with the surface structure, formed after heating the crystal in the range $T = 350$-550°C.

The intensity of the ring structure increases with increasing temperature and heating time, while the intensity of the substrate pattern decreases. The presence of this surface structure at only low electron energies again indicates that it is the property of the surface. Such a ring pattern could be due to a disordered surface structure which is rotated about the [100] axis.

In order to prove that the surface structures are the property of the clean platinum surface, several experiments were performed.

The platinum surface which exhibits the domain structure was heated in oxygen (2×10^{-6} Torr) at 440°C. This treatment gave rise to the formation of the rotated oxygen structure reported by Tucker[5] which coexists with the domain structure. Heating the crystal above

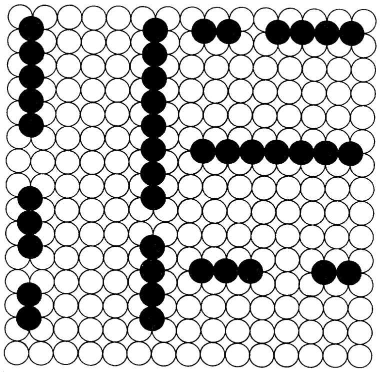

FIG. 2. Model of the proposed domain structure.

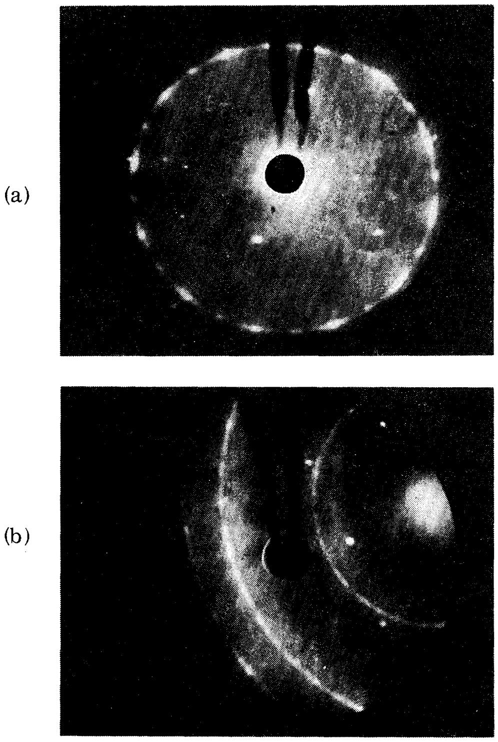

FIG. 3. Segmented ring (a) and completed ring (b) "disorder" surface structures of the (100) face formed after heating the crystal in the range $T = 750$–1769°C.

750°C in oxygen resulted in the appearance of the ring structure. Both surface structures appear to be unaffected by the presence of oxygen.

The platinum surface which exhibits the domain structure was heated in hydrogen ($\approx 2 \times 10^{-6}$ Torr) at 500°C. This treatment had no effect upon the diffraction pattern. The ring structure appeared when the crystal was heated in hydrogen at higher temperatures (>750°C).

Changing the conditions used for ion bombardment (argon, xenon, ion voltage, ambient pressure) had no effect upon the surface characteristics. The ring structure was also obtained without ion bombardment by heating the crystal to temperatures $T > 750°\mathrm{C}$. The domain structure could not be obtained without ion bombardment. Heating the crystals to a temperature which corresponds to the stability range of the observed domain structure was inadequate to anneal the surface damage produced by our crystal preparation.

Using several crystals in all our experiments has not affected the reproducibility of the results. Therefore, it appears unlikely that impurities may be the cause of the observed surface structures.

Detailed investigations of these surface structures, of their kinetics of formation, are in progress and will be reported later. The catalytic properties of platinum and the temperature sensitivity of the catalytic activity[6] seems also to support our findings of the existence of different surface structures as a function of the thermal history of platinum single crystals.

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INSULATING FERROMAGNETIC SPINELS

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All previously known magnetic compounds having the spinel structure, except for one single compound, have spontaneous moments which are consistent with ferrimagnetic or more complex spin configurations. We report herein a family of chalcogenide spinels, typified by the compounds $CdCr_2S_4$, $CdCr_2Se_4$, $HgCr_2S_4$, and $HgCr_2Se_4$, which are both electrical insulators and ferromagnetic. The pertinent characteristics of these ferromagnetic compounds are given in Table I (all data taken on polycrystalline samples). The data for the similar compounds $ZnCr_2S_4$ and $ZnCr_2Se_4$, which are antiferromagnets, are also included in Table I for

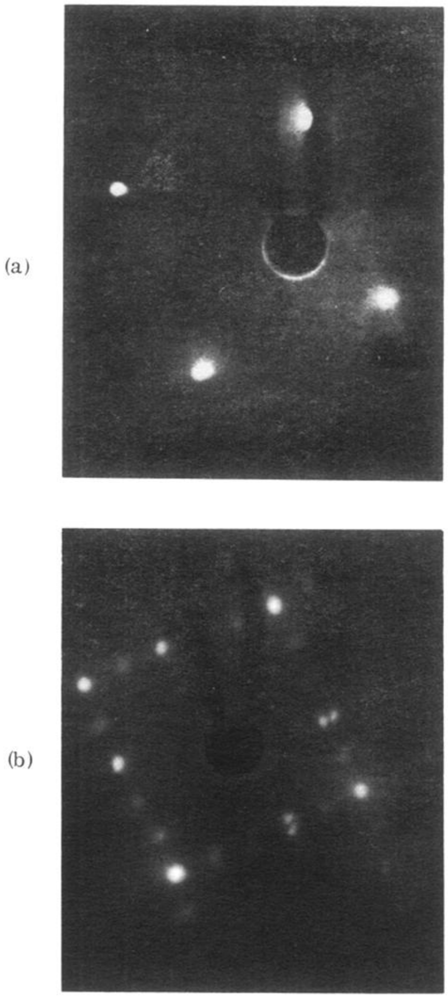

FIG. 1. (a) Diffraction pattern of clean platinum (100) surface at $E = 58.0$ eV. (b) Pattern ($E = 58.0$ eV) of the (100) face with the surface structure, formed after heating the crystal in the range $T = 350$–550°C.