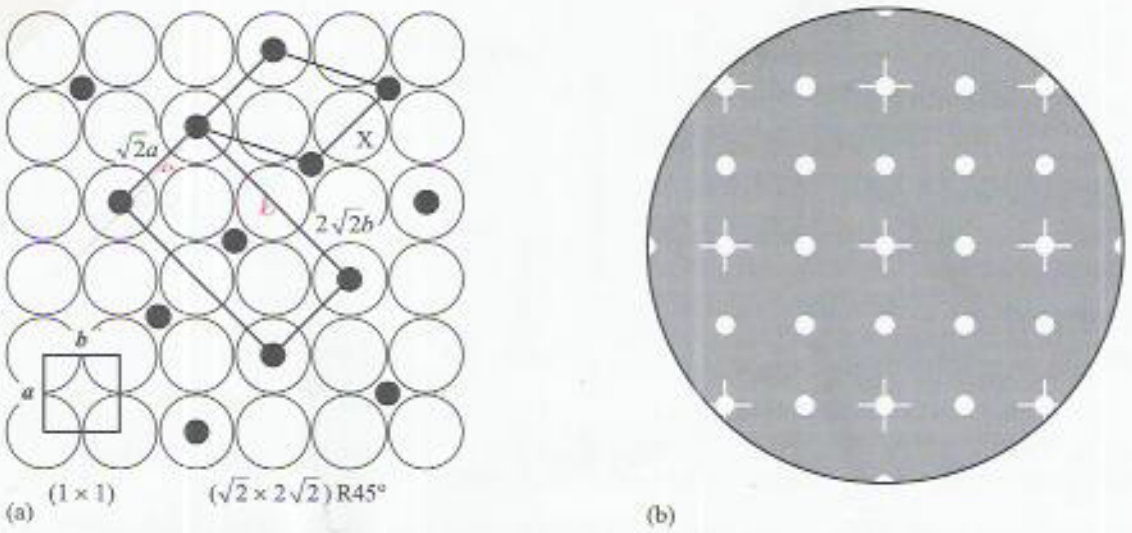


**Figure 2** (a) Structure of the adsorbed layer formed on Pd(100) by exposure to NO(g) at 100 K and heating to 250 K; large open circles represent top layer Pd atoms, and small filled circles represent adsorbate species. (b) Spot positions in the LEED pattern observed on further heating to 450 K; crosses mark positions that would be occupied in the pattern from a clean Pd(100) surface.

(c) (*8 marks*) As the surface temperature is increased from 100 to 250 K, a sharp LEED pattern develops, which can be interpreted in terms of the Pd(100)$(\sqrt{2} \times 2\sqrt{2})$R45° structure in Figure 2a.

(i) Calculate the NO fractional surface coverage at 250 K.

(ii) Noting that the vectors defining any *valid* unit mesh must join points on a surface that are *identical in every respect*, explain why the 'mesh' X in Figure 2a does not properly represent the repeating nature of the surface geometry, whereas the $(\sqrt{2} \times 2\sqrt{2})$R45° mesh does. (*50–100 words*)

(iii) Construct a diagram showing the positions of spots in the LEED pattern for the Pd(100)$(\sqrt{2} \times 2\sqrt{2})$R45° system at 250 K, and identify those positions at which spots would occur in the pattern from a clean Pd(100) surface.

(d) (*6 marks*) With further increases in surface temperature, a second sharp LEED pattern (Figure 2b) develops at 450 K. Use the information provided by this pattern to identify the real surface structure in terms of the $(m \times n)$ notation, giving your reasoning.

On a sketch of a Pd(100) top surface layer, show one possible arrangement of NO molecules in this surface structure.

Discuss briefly any details of the structure that remain uncertain and suggest additional LEED information which could be used to resolve the difficulty. (*50–100 words*)

**Question 3**

*This question carries 35% of the marks for this assignment, and tests Objectives 1, 3 and 6 of Block 5 and Objectives 1, 2, 4, 5 and 7 of Topic Study 2, Part 1.*

(a) (*16 marks*) Considering the mixture of nitric oxide (NO) and nitrogen dioxide ($NO_2$) represented conventionally as $NO_x$, summarize carefully (i) the reactions responsible for its generation as a result of the operation of internal combustion engines, and (ii) the harmful effects it may have in the environment, both directly and by its involvement in the production of other pollutants.

*Your answer should be logically structured and concise, not exceeding 500 words, and should include relevant equations. Up to* ***3 marks*** *will be awarded for a clear, concise and logical style.*

(b) (*6 marks*) Describe briefly the way in which the composition of the exhaust gases leaving a combustion engine operating under *net oxidizing* conditions varies with the air : fuel (A/F) ratio (a diagram *is not* required). Hence, discuss briefly why the three-way catalytic converter is unsuitable for use with engines of the 'lean burn' type. (*100–150 words*)

(c) (*13 marks*) A recent attempt to overcome the problem of $NO_x$ emissions from lean-burn engines examined an arrangement of two successive catalysts beds, the first containing platinum supported on activated carbon, which gives very high NO conversion at 200 °C. The reaction, however, proceeds via two parallel routes: complete reduction of NO to $N_2$ and partial reduction to nitrous oxide, $N_2O$. At 200 °C, the second of these processes predominates, generating significant amounts of $N_2O$, undesirable as a contributor to both stratospheric ozone depletion and the greenhouse effect. Thus, the catalyst in the second bed is required to have high activity for $N_2O$ reduction to $N_2$. Of various potential candidates, the most promising were found to be cobalt-rhodium supported on the mineral hydrotalcite (Co-Rh/Ht) and the iron form of the zeolite ZSM5 (Fe-ZSM5).

(i) It was found to be advantageous to inject propene, $C_3H_6$, at low concentration into the exhaust stream as it entered the second catalyst bed. $N_2O$ conversion into $N_2$ under these conditions over Co-Rh/Ht and Fe-ZSM5 is shown as a function of temperature in Figure 3a. Identify which of the two catalysts is the more efficient, discussing briefly the reason(s) for your choice. (*about 10 words*)