

## A Study of the Sites Involved in the Chemisorption of Hydrogen on $\text{Co}_3\text{O}_4$ by Magnetic and Nuclear Neutron Diffraction

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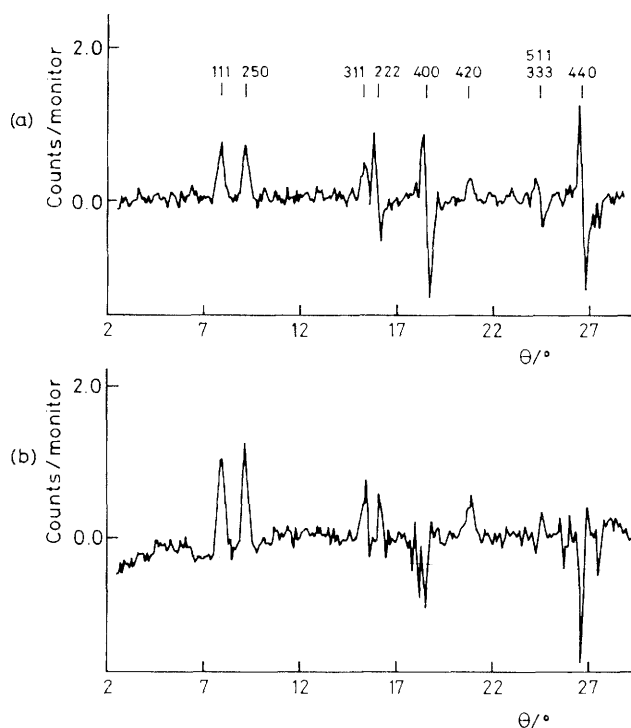
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$\text{D}_2$  dissociates on  $\text{Co}_3\text{O}_4$  at room temperature but not at 40 K, and donates electrons to  $\text{Co}^{3+}$  defects in tetrahedral sites.

The experiments reported here on the chemisorption of hydrogen on  $\text{Co}_3\text{O}_4$  were carried out on the powder diffractometer D1B. The sample, procedure, and data treatment were as for the physisorption experiment reported previously.<sup>1</sup>

The sample was cooled to 20 K under vacuum and diffraction pattern 1 was obtained. The sample was then warmed to 40 K and  $\text{D}_2$  was introduced and adsorbed. Diffraction pattern 2 was obtained, again at 20 K. Finally, the sample was

warmed to room temperature. All the  $\text{D}_2$  was desorbed above 120 K as expected<sup>2</sup> and began to re-adsorb at temperatures above 270 K. The amount of  $\text{D}_2$  adsorbed the second time was equal to that of the first adsorption. Diffraction pattern 3 was then obtained at 20 K. The diffraction difference patterns 2 – 1 and 3 – 1 were calculated and are shown in Figure 1. The supplementary attenuation of the neutron flux due to  $\text{D}_2$  was negligible.



**Figure 1.** (a) Diffraction difference pattern 3-1 (room temperature). (b) Diffraction difference pattern 2-1 (low temperature).

The neutron diffraction pattern of the bare solid has been studied by Roth.<sup>3</sup> The interaction of neutrons with nuclei contributes to all the peaks except 200 and 420. The magnetic interaction of the neutrons with the anti-ferromagnetic lattice of unpaired electron spins of  $\text{Co}^{2+}$  in tetrahedral sites contributes to the 111, 200, 113, 222, 331, and 420 peaks. The difference patterns show Bragg peak modifications (BPM) but no surface peaks.

$A_C$  and  $A_F$  are the amplitudes of the peaks scattered by the bare crystal and the adsorbate, respectively. The BPM are due to cross terms  $A_C A_F$ .<sup>4</sup> Magnetic and nuclear interactions are distinguished by an additional index M or N, respectively. The BPM with magnetic terms are given in equation (1).  $\langle \rangle$  in-

$$\begin{aligned} \text{BPM} &= \langle (A_{CM} + A_{CN})(A_{FM} + A_{FN}) \rangle \\ &= \langle A_{CM} A_{FM} \rangle + \langle A_{CM} \rangle A_{FN} + A_{CN} \langle A_{FM} \rangle + \\ &\quad A_{CN} A_{FN} \end{aligned} \quad (1)$$

icates the average of the neutron spin orientations operating only on magnetic amplitudes. For unpolarized neutrons  $\langle A_{CM} \rangle = \langle A_{FM} \rangle = 0$ . For purely magnetic peaks such

as 200 and 420  $A_{CN} = 0$ . Only  $\langle A_{CM} A_{FM} \rangle$  is non-zero. The BPM of purely magnetic peaks with unpolarized neutrons are due only to magnetic modifications of the surface.

Contact potential measurements show that on chemisorption  $\text{D}_2$  donates electrons to the solid.<sup>5</sup> These can be accepted only by  $\text{Co}^{3+}$  as  $\text{Co}^{4+}$  and  $\text{Co}^+$  do not exist under these conditions. The modified cations are close to the surface because the negative space charge produced is attracted by the positive chemisorbed layer. Thus, the theory of BPM shape developed for physisorption<sup>1,4</sup> applies here. The conclusions of the theory are simple for 200 and 420: magnetic moments in tetrahedral sites give a BPM with a symmetry axis at  $\theta = \theta_0$  whereas in octahedral sites a symmetry centre is obtained.

Figure 1 shows that 200 and 420 peaks have a symmetry axis {400 on pattern 3-1 [Figure 1(a)] is an example of a peak with a symmetry centre}. Thus,  $\text{Co}^{3+}$  ions in tetrahedral sites ( $\text{Co}_T^{3+}$ ) exist before chemisorption and are transformed into  $\text{Co}^{2+}$ . The presence of  $\text{Co}_T^{3+}$ , unexpected in a normal spinel, may be due to the particular preparation of  $\text{Co}_3\text{O}_4$  used to obtain high specific area. The BPM corresponds to an increase of scattering power. This means that  $\text{Co}_T^{3+}$  ions are low spin or, if they are high spin, are less coupled to the antiferromagnetic lattice than  $\text{Co}^{2+}$ , the overlap of the 3d orbitals with the  $\text{O}^{2-}$  p orbitals, responsible for superexchange, being smaller for  $\text{Co}_T^{3+}$  than for  $\text{Co}_T^{2+}$ . If octahedral  $\text{Co}^{2+}$  ions are created by chemisorption, they will be seen only if they are coupled to the antiferromagnetic lattice. To conclude that all electrons go to tetrahedral sites would require a quantitative analysis which is not yet possible.

Nuclear Bragg peaks are all modified by room-temperature chemisorption (RTC) whereas only low-angle peaks up to 440 are modified for low-temperature chemisorption (LTC). The interpretation of this is that for RTC,  $\text{D}_2$  is dissociated and D bound to O occupies a well-defined position, whereas for LTC  $\text{D}_2$  molecules or ions can adopt many orientations, giving rise to a molecular form factor. Accordingly the electron transfer for RTC would be expected to be double that for LTC. This again would require a quantitative analysis of data for confirmation.

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