J. Synchrotron Rad. (1995). 2, 312–314

Photoemission Study of CO Adsorption on Gd

C. Searle,[a] R. I. R. Blyth,[a] R. G. White,[b] N. P. Tucker,[a] M. H. Lee[a] and S. D. Barrett[b]

[a]Surface Science Research Centre, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK, and [b]Department of Physics, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

(Received 25 April 1995; accepted 14 August 1995)

Angle-resolved UV photoemission spectroscopy has been used to investigate the interaction of CO with Gd films, grown on W(110). The results suggest that CO adsorbs dissociatively, initially forming Gd_2O_3, with subsequent catalytic oxidation of CO to form carbonate.

Keywords: photoemission; CO on Gd/W(110); angle-resolved UV photoemission spectroscopy; LEED.

1. Introduction

There has been much recent photoemission work (Li, Zhang, Dowben & Onellion, 1993; Vescovo, Rader, Kachel, Alkemper & Carbone, 1993; Navas, Starke, Laubschat, Weschke & Kaindl, 1993) on rare-earth thin films grown on the (110) surfaces of refractory metals, particularly W. These films are crystalline, and yield low-energy electron diffraction (LEED) patterns with hexagonal symmetry. By convention, these films are described as (0001) surfaces, implying an h.c.p. structure. However, this designation is provisional since qualitative LEED cannot determine three-dimensional structure. The majority of rare-earth thin-film studies have been of the clean surfaces; there have been very few studies of the interaction of adsorbates with single-crystal rare-earth surfaces. Early studies of adsorption on rare-earth metal surfaces were motivated by the large hydrogen uptake of these metals, with a parallel interest in possible catalytic applications. Studies were largely of evaporated polycrystalline films, and used combinations of work-function methods (Surplice & Brearley, 1978; Strasser, Bertel & Netzer, 1983) and UV photoemission (Netzer & Bertel, 1982). This paper presents the results of synchrotron radiation photoemission studies for low exposures of CO adsorbed onto Gd/W(110).

2. Experimental

The experiment was performed on the Liverpool/Manchester photoemission beamline (4.1) (Dhanak, Robinson, van der Laan & Thornton, 1992) at the SRS, Daresbury Laboratory. A Vacuum Science Workshop HA54 hemispherical analyser was used, with an overall resolution at $h\nu = 40$ eV of 0.2 eV. The vacuum chamber, with a base pressure $< 10^{-10}$ mbar, was fitted with Vacuum Generators LEED optics. The W(110) substrate was prepared by roasting at 1400 K in 10^{-6} mbar oxygen to remove carbon, followed by periodic flashing to > 2000 K to remove residual O and H, until the surface showed a sharp 1 × 1 LEED pattern. Cleanliness of the surface was verified by measuring the W $4f_{7/2}$ surface core-level shift, which is known to be highly sensitive to contamination (Riffe, Wertheim & Citrin, 1989).

Gd was evaporated from a water-cooled W-wire evaporator (Dowben, LaGraffe & Onellion, 1989) with the substrate held at room temperature to ensure layer-by-layer growth (Kolaczkiewicz & Bauer, 1986). The pressure remained below 4×10^{-10} mbar during evaporation. Film growth was monitored by UV photoemission spectroscopy until features from the substrate valence band were not detectable. CO (Gas Distillers, 99.997% pure) was dosed by backfilling the chamber, with the gas purity checked using a Vacuum Generators residual gas analyser.

3. Results and discussion

A spectrum from a Gd film (as grown) is shown in Fig. 1. This is in good agreement with previously published spectra of Gd on W(110) (Li *et al.*, 1993). The sharp peak (0.5 eV FWHM) near the Fermi level (E_F) is attributed to a surface state, with its intensity indicating the single-crystal nature of the film. The properties of the surface state have been thoroughly reviewed by Vescovo *et al.* (1993). The 8.4 eV peak is due to emission from the Gd $4f$ states and has a FWHM of 1.5 eV. The nature of the valence-band feature at 1.6–1.7 eV is disputed; while Vescovo *et al.* (1993) consider the feature to be due to a surface resonance, Li *et al.* (1993) assign the emission to Gd $5d$ bulk bands. The peak at 5.8 eV is attributed to oxygen $2p$ orbitals from residual contamination. By comparison with the oxygen-dosing results of Vescovo *et al.* (1993), we estimate the level of oxygen contamination to be <3%.

Fig. 2 shows a series of spectra for a Gd film dosed with CO at room temperature. Spectra for the CO exposure sequence (Fig. 2) show no features with binding energy of 10 eV or higher. Since the 4σ orbital of molecularly adsorbed CO is known to have a binding energy of ~10.6 eV (Miranda, Wandelt, Rieger & Schnell, 1984, and references therein), the absence of emission in this region implies dissociative adsorption of CO, which is consistent with previous work-function (Strasser *et al.*, 1983) and X-ray photoemission (Affrossman, 1981) studies of CO adsorbed on Sc, Er and Yb. Prior UV photoemission spectroscopy studies have also reported O_2 and H_2 adsorbing dissociatively on Gd (Vescovo *et al.*, 1993; Li *et al.*, 1993; Zhang, Dowben, Li & Onellion, 1995). The spectra show noticeable similarities with UV photoemission spectroscopy studies of oxygen-dosed Gd films: increased emission from the oxygen 2p orbitals and a quenching of the valence-band features between E_F and 1.7 eV as a sesquioxide-like surface forms (Vescovo *et al.*, 1993). At exposures of 1.4 L and above, the 4f emission shows increased spectral weight on the high-binding-energy side, consistent with the formation of Gd_2O_3 (Vescovo *et al.*, 1993). At these higher exposures a new broad emission feature is seen with peak intensity at 2.4 eV. Since it is known that rare-earth sesquioxides catalyse the conversion of CO to CO_2, forming stable carbonates at the surface (Netzer & Bertel, 1982), it is possible that this feature is due to the presence of a carbonate species. There have been no previous UV photoemission studies of CO on rare-earth metals. Gouder, Colmenares, Naegele, Spirlet & Verbist (1992), however, performed a UV photoemission spectroscopy study of CO adsorption on polycrystalline U, which has a related electronic structure to Gd (being in the same column of the Periodic Table). They found that CO adsorbs dissociatively, with an emission at 2.4 eV attributed to carbon 2p orbitals.

We also note that the adsorption of CO does not produce a peak at a binding energy of ~9.6 eV. Previous photoemission studies of bulk single-crystal rare earths (Barrett, 1992) show an intense surface-order-dependent state at a binding energy of ~9.6 eV. It has been suggested (Bodenbach, Hohr, Laubschat, Kaindl & Methfessel, 1994) that this feature is in some way due to contamination. The results in this work, together with those of Vescovo *et al.* (1993) and Li *et al.* (1993), do not support this argument, as they show that CO, H and O do not produce adsorbate peaks at binding energies > 7 eV.

4. Conclusions

The absence of any molecularly adsorbed CO emission features implies that CO is dissociatively adsorbed onto Gd. It is possible that surface carbonates form with CO exposures > 1 L due to the catalytic activity of the surface oxide phase. There is no emission from the adsorbed overlayer that can be correlated with the surface-order-dependent state feature of bulk single-crystal rare earths.

CS, RGW and NPT acknowledge receipt of EPSRC studentships. We thank Dr A. W. Robinson and Mr D. Collister for technical assistance, and Professor P. A. Dowben

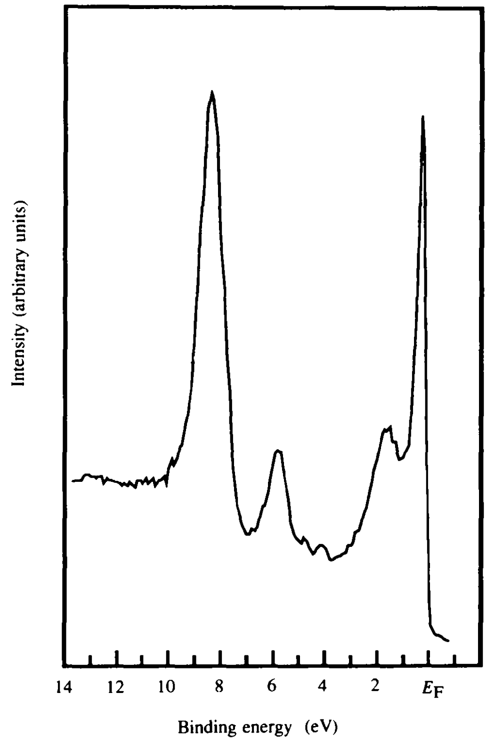

Figure 1
Angle-resolved photoemission spectrum of Gd/W(110). $h\nu$ = 40 eV, incidence angle 40°, normal emission.

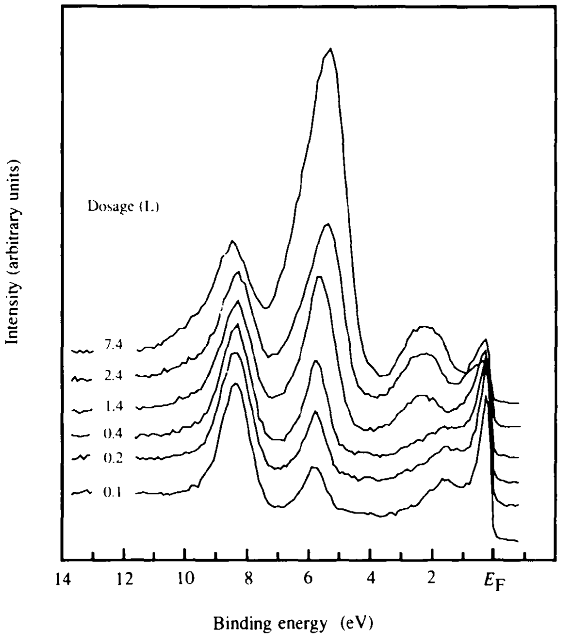

Figure 2
Angle-resolved photoemission spectra of Gd/W(110) exposed to CO. $h\nu$ = 40 eV, incidence angle 40°, normal emission.

(University of Nebraska) for the loan of the evaporator. This work was funded by EPSRC and we are grateful for their support.

References

Affrossman, S. (1981). *Surf. Sci.* **111**, 1–10.

Barrett, S. D. (1992). *Surf. Sci. Rep.* **14**, 271–354.

Bodenbach, M., Hohr, A., Laubschat, C., Kaindl, G. & Methfessel, M. (1994). *Phys. Rev. B*, **50**, 14446–14451.

Dhanak, V. R., Robinson, A. W., van der Laan, C. & Thornton, G. (1992). *Rev. Sci. Instrum.* **63**, 1342–1345.

Dowben, P. A., LaGraffe, D. & Onellion, M. (1989). *J. Phys. Condens. Matter*, **1**, 6571–6587.

Gouder, T., Colmenares, C. A., Naegele, J. R., Spirlet, J. C. & Verbist, J. (1992). *Surf. Sci.* **264**, 354–364.

Kolaczkiewicz, J. & Bauer, E. (1986). *Surf. Sci.* **175**, 487–507.

Li, D., Zhang, J., Dowben, P. A. & Onellion, M. (1993). *Phys. Rev. B*, **48**, 5612–5620.

Miranda, R., Wandelt, K., Rieger, D. & Schnell, R. D. (1984). *Surf. Sci.* **139**, 430–442.

Navas, E., Starke, K., Laubschat, C., Weschke, E. & Kaindl, G. (1993). *Phys. Rev. B*, **48**, 14753–14755.

Netzer, F. P. & Bertel, E. (1982). *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 5, edited by K. A. Gschneidner Jr & L. Eyring, pp. 217–317. Amsterdam: North Holland.

Riffe, D. M., Wertheim, G. K. & Citrin, P. H. (1989). *Phys. Rev. Lett.* **63**, 1976–1979.

Strasser, G., Bertel, E. & Netzer, F. P. (1983). *J. Catal.* **79**, 420–430.

Surplice, N. A. & Brearley, W. (1978). *Surf. Sci.* **72**, 84–94.

Vescovo, E., Rader, O., Kachel, T., Alkemper, U. & Carbone, C. (1993). *Phys. Rev. B*, **47**, 13899–13902.

Zhang, J., Dowben, P. A., Li, D. & Onellion, M. (1995). *Surf. Sci.* **329**, 177–183.

Short Communications

J. Synchrotron Rad. (1995). **2**, 315–316

Sample housing for high-energy Compton measurements

Ch. Bellin, J. Frouin and G. Loupias

Laboratoire de Minéralogie-Cristallographie, Université Pierre et Marie Curie, Case 115, 4 place Jussieu, 75252 Paris CEDEX 05, France, and LURE, Université Paris Sud, Bâtiment 209D, 91405 Orsay CEDEX, France

(*Accepted 14 August 1995*)

In order to obtain reliable Compton spectra using high-energy photons, the scattered beam must be free of parasitic photons, because of the weakness of the double-differential inelastic cross section. The purpose of the device presented in this paper is to remove photons scattered by air, the sample holder or any other stopper. It has been tested on ESRF beamline 2, which is devoted to materials science.

Keywords: inelastic scattering; high-resolution spectrometer; low noise; Compton scattering; sample housing.

1. Introduction

Inelastic scattering of photons is a powerful tool for investigating the electron densities of solids (Cooper, 1985; Platzman, 1989). The Compton profile is easily related to the double-differential cross section of scattered photons (energy and direction analysis). Nevertheless, photoelectric absorption strongly competes with inelastic scattering (Evans, 1955) in samples with large Z. Therefore, the first high-resolution Compton spectrometer using synchrotron radiation (Loupias & Petiau, 1980) was limited to the study of light elements owing to the low critical energy (roughly 8 keV) of the superconducting wiggler of LURE/DCI (Orsay, France). For inelastic scattering experiments, a major improvement to the new generation of synchrotrons, such as the ESRF, is the increase in photon energy, mainly as a result of the high electron energy in the ring and the use of wigglers as insertion devices. A typical energy of 29 keV is delivered by the wiggler of ID 11. Furthermore, the optics of beamline 2 are designed in order to obtain a small spot size of $0.2 \times 0.2\,\text{mm}^2$ on the sample. As a consequence, a large range of materials (with large Z and small crystal size) may be studied as long as a dispersive analysing device is installed on the main arm of the κ diffractometer (Kvick, 1994).

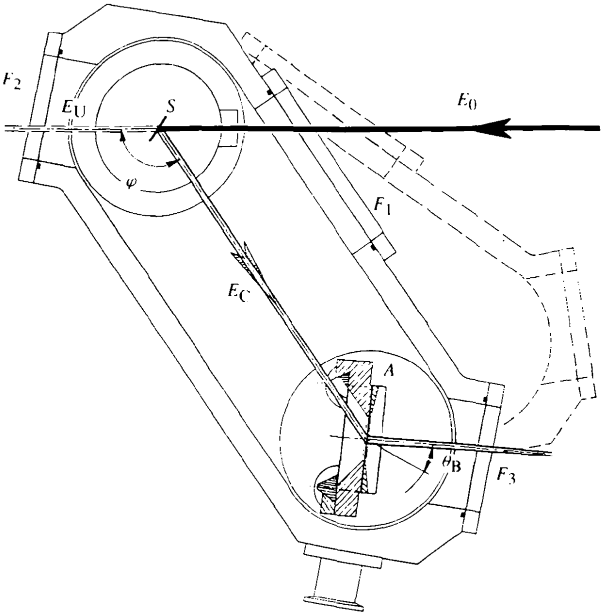

Figure 1
Sample and analyser housing.

2. Description

Using such a set-up, the photons, scattered by the sample S at an angle φ of between 125 and 145°, are energy analyzed and focused by a Cauchois curved crystal A (Cauchois, 1932) on a position-sensitive detector (image plate or gas detector).

At high energies, the system is very sensitive to parasitic photons scattered by air and any material in the beam paths. Such photons are also energy analysed by the crystal analyser and give a contribution to the Compton profile of interest. A special housing for the sample and analyser has been designed in order to refine experimental conditions, fulfilling the following conditions:

(1) The sample and analyser are under vacuum in order to avoid the parasitic contribution of air-scattered photons.

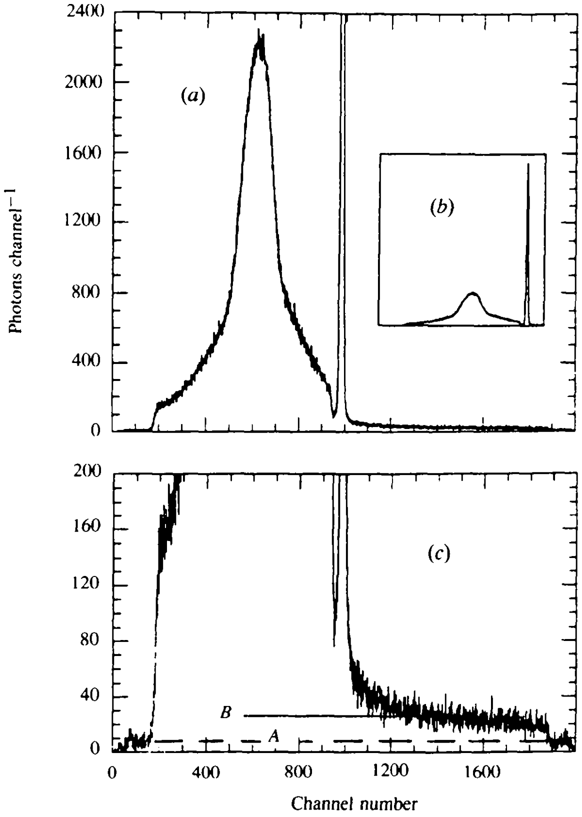

Figure 2
(*a*) Compton peak of the silicon direction [111] with the thermal peak on right side, (*b*) full-scale Compton and thermal peaks, and (*c*) expanded view of (*a*) showing details of backgrounds (*A* and *B*).