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AZIMUTHALLY-DEPENDENT X-RAY ABSORPTION NEAR EDGE STRUCTURE FOR SULPHUR ADSORBED ON NICKEL (110)

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Abstract

The X-ray absorption near edge structure (XANES) for S atoms in a half-monolayer coverage on the (110) surface of nickel shows a strong azimuthal dependence, not previously reported for an atomic adsorbate. The near edge resonance is shown by calculations to be determined in a complicated way by several shells of neighbouring atoms, and is not simply dominated by sulphur-nickel near neighbour scattering.

The adsorption of sulphur onto the low-index planes of nickel has been one of the most studied systems in modern surface science. In our surface X-ray absorption investigations (to be published), we have noted a striking azimuthal dependence in the XANES spectra for Ni(110)c(2x2)S. There is a marked difference between the near edge spectra when the \underline{E} vector is aligned along the two principal azimuths, [100] and [1 $\bar{1}$ 0] (Fig. 1(a) and (b)). Such a difference might be expected in view of the asymmetry of the face-centred cubic (110) surface, but we are not aware of any prior observations for an atomic adsorbate. For instance, oxygen on Cu(110) [1] or Ag(110) [2] (where the adsorption site is the two-fold bridge in the [100] direction) does not show a marked effect. A strong azimuthal dependence of XANES has previously been reported for the formate molecule adsorbed on Cu(110) [3], but here the XANES structure derives from intramolecular resonances within the oriented formate molecule itself, rather than scattering involving the metal substrate atoms.

Surface X-ray absorption spectra were measured using apparatus at the Daresbury Laboratory Synchrotron Radiation Source [4], with the absorption coefficient above the S K-edge at around 2470eV being recorded by collecting the S KLL Auger electrons with a cylindrical mirror analyser. Normalisation to the incident photon flux was achieved by monitoring the drain current of a thin Al foil placed between the monochromator and the sample. Spectra were recorded with the incident photon beam close to the sample normal and with the \underline{E} vector of the plane polarised light aligned parallel to the [100] and [1 $\bar{1}$ 0] azimuths. The sample was cleaned by the usual methods of Ar⁺ bombardment and heating in oxygen, and surface cleanliness and order were checked with Auger electron spectroscopy and LEED. Sulphur dosing was performed by exposure of the clean nickel surface to 8 Langmuirs (1 Langmuir=1x10⁻⁶ Torr.sec) of H₂S gas, followed by briefly heating the sample to 200°C. This formed a c(2x2) structure giving a sharp LEED pattern.

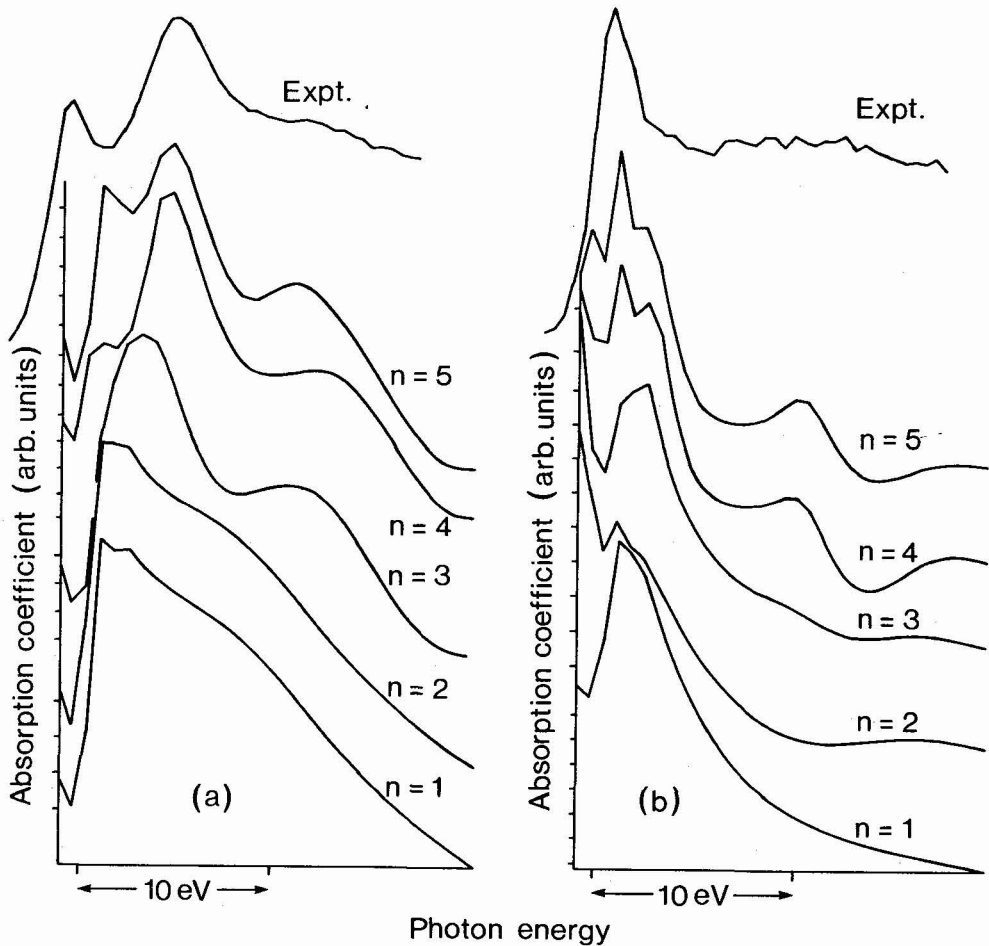


Fig.1. Experimental and calculated sulphur K-edge near-edge structure for $\text{Ni}(110)_c(2 \times 2)\text{S}$, with photons normally incident, and their polarisation vector aligned along (a) the $[100]$ and (b) the $[1\bar{1}0]$ azimuth.

In order to try to understand the detailed origin of the azimuthal dependence, we have performed calculations of the XANES using the cluster-based multiple scattering scheme developed at Daresbury [5]. The atoms are arranged into 'shells' around the central (absorbing) S atom, with all atoms at a similar radial distance being lumped into one shell, and the full multiple scattering equations solved within each shell and between all shells. The results of these calculations are also given in Fig. 1, showing the effect of adding further shells of atoms around the central S atom, which is known [6-8] to adsorb in the twofold (rectangular) hollow site. Although a marked asymmetry in the XANES is found even for one shell of atoms (just the four near neighbour atoms in the rectangular unit), it is seen that as many as five shells (containing 42 atoms) influence the spectra. The agreement with experiment is qualitatively reasonable, showing the same trends in azimuthal dependence, although quantitative agreement is lacking. This may not be too surprising since the details of the surface potential are not included in the calculation. The main change in the calculated XANES curves occurs with the inclusion of the third shell, which contains the next sulphur adsorbate atoms as

well as ten nickel atoms. We have established (by performing this calculation with these sulphur atoms omitted) that they in fact produce a negligible effect, and so the major effects on the XANES are from the nickel substrate atoms alone.

It might have been hoped that the XANES would be dominated by the near neighbour interaction. This would encourage the view that XANES spectra could be used to 'fingerprint' atomic adsorption sites, for instance on disordered surfaces. The asymmetry shown by the calculated spectra for just four nickel neighbours could be of some importance in this respect. Nevertheless it is disappointing that the XANES turns out to be a complicated function of the geometry and electron scattering factors of as many as 42 atoms. This is essentially the same result as was found for the Ni(001)c(2x2)O system [9], and contrasts with the XANES of molecular adsorbates, where the near-edge structure has been shown by experimental observations [10] and calculations [11] to be a very short-range phenomenon, being largely dominated by intramolecular scattering.

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