X-Ray Photoelectron Diffraction: a Novel Method of Structural Analysis in Complex Monocrystalline Solids

By JOHN M. ADAMS, STEPHEN EVANS,* and JOHN M. THOMAS†
(*Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed* SY23 1NE)

Summary The unique value of *X*-ray photoelectron diffraction phenomena in determining substitutional patterns in complex monocrystalline solids is demonstrated in studies of naturally occurring layered aluminosilicates.

IT has for some years been recognised that photoelectrons generated below the surface of a single-crystal specimen may be elastically scattered (diffracted) before their escape from the solid,[1] although, in the absence of both adequate quantitative interpretation[2] and any chemical application, interest in the phenomenon has hitherto remained relatively slight. We report the first such application, indicating how *X*-ray photoelectron diffraction (XPD) data can be used in an attractively direct manner to derive new structural information, very difficult to obtain from established techniques.

We have recently recorded *X*-ray photoelectron spectra (XPS) of several vacuum-cleaved micas as a function of electron takeoff angle. In the Figure we show the angular

---

† Address as from April 1978: Department of Physical Chemistry, University of Cambridge, Cambridge CB2 1EP.

TABLE. XPD range data for micas

Description of ratio by site symmetries	Mean range of variation[a] (S.D.)	No. of examples averaged	Representative examples (in muscovite, see text and the Figure)
Between core-levels in atoms at different, unique sites	25 (3)	7	Si2*p* : K2*p*
Between one core-level in atoms at several sites and another in atoms at different, unique sites	18 (2)	4	Si2*p* : O1*s*
Between two core-levels in same atom	6 (2)	8	K2*p* : K3*p*, Si2*p* : Si2*s*

[a] Appreciable changes in the electron acceptance angle may affect the magnitude of the range observed; these data were taken with an AEI ES 200A electron spectrometer.

variation of the principal XPS intensity ratios for muscovite, a typical mica. (Qualitatively similar results were obtained from the other materials examined.) Now, *a priori*, a number of factors might be expected to be important in determining XPD patterns from a given crystal in a fixed azimuthal orientation: these include (i) the location (site symmetry) of the ionised atom, (ii) the wavelength, λ, of the photoelectron, and (iii) the radius of the ionised shell. However, every intraelemental ratio examined (*e.g.*, K2*p* : K3*p* and Si2*p* : Si2*s* in the Figure) has been found to remain essentially invariant with angle, showing clearly that both differences between the photoelectron wavelengths ($<$ *ca.* 30%), and between the radii of the shells ionised, are very much of secondary importance in determining the overall range of values of a peak area ratio. Consequently, we are able to correlate (Table) the overall ranges of variation of each ratio directly with the differences between the atomic sites of each pair of core-levels.

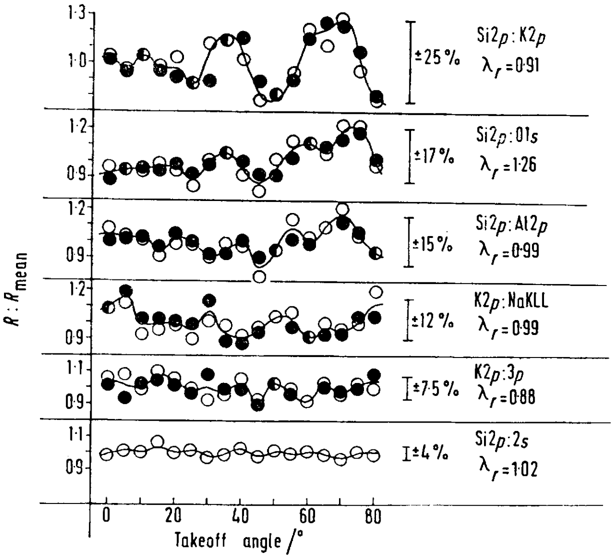

FIGURE. Normalised XPD patterns for muscovite. The take-off angle is defined as the angle between the electron beam and the normal to the surface of the specimen. Filled and open circles distinguish data from two different cleavages in the same specimen; λ_r denotes the ratio of the de Broglie wavelengths of the electrons concerned. The crystal structure of muscovite is described fully in ref. 4.

The Figure includes examples of each category of ratio listed. The principal interlamellar cation in muscovite, potassium, occupies central sites quite distinct from those of the tetrahedrally-co-ordinated silicon atoms, so that the range of variation is at its widest in the Si2*p* : K2*p* ratio. Oxygen is present in three distinct environments in these minerals[3,4] so that the O1*s* XPD pattern is partly 'averaged-out'; the ratio Si2*p* : O1*s* thus varies much less than Si2*p* : K2*p*.

The excess aluminium present in muscovite over the proportion required to fill two-thirds of the octahedral sites is believed to replace silicon in tetrahedral co-ordination, although the evidence for this is largely circumstantial.[3,4] The XPD data for these elements are therefore of particular interest. The considerable reduction in the range of the Si2*p* : Al2*p* ratio in muscovite relative to that for Si2*p* : K2*p* suggests directly (*cf.* discussion of Si2*p* : O1*s* above) that such substitution does indeed occur in muscovite, a conclusion reinforced by the behaviour of this ratio in related minerals. In phlogopite, which is believed to contain aluminium only in substitution for tetrahedral silicon, Si2*p* : Al2*p* is essentially constant (range ±4%), while in lepidolite it varies by ±24%; most of the aluminium in this latter mineral is octahedrally rather than tetrahedrally co-ordinated.

Photon-excited Auger spectra can be used interchangeably with the primary photoelectron spectra in these studies. Thus the variation of the K2*p* : Na*KLL* Auger intensity ratio, substantially greater than would be expected if Na and K occupied identical sites, may be interpreted as indicating that in muscovite, as in montmorillonite,[5] the smaller ion is not located mid-way between the layers, but is displaced to achieve more effective co-ordination to the oxygen hexagons within each layer. Sodium comprises only *ca.* one-tenth of the interlayer ion in this muscovite, and is more or less randomly distributed; conventional diffraction techniques are therefore powerless to reveal even its approximate location.

The potentialities of XPD for the study of substitutional impurities in minerals are thus clearly considerable, although the technique is by no means confined to geochemistry. Much further work will, however, be required to delineate fully all the areas within which XPD will prove valuable.

We thank the S.R.C. for support.

(*Received*, 1*st December* 1977; *Com.* 1227.)

---

[1] K. Siegbahn, U. Gelius, H. Siegbahn, and E. Olson, *Phys. Letters* (*A*), 1970, **32**, 221; *Physica Scripta*, 1970, **1**, 272; C. S. Fadley and S. Å. L. Bergström in 'Electron Spectroscopy,' ed. D. A. Shirley, North Holland, Amsterdam, 1971, p. 233; *Phys. Letters* (*A*), 1971, **35**, 375; S. Evans, *Proc. Roy. Soc. A*, 1978, in the press; C. S. Fadley, *Progr. Solid State Chem.*, 1976, **11**, 265.

[2] K. Siegbahn, UUIP (Uppsala University Institute of Physics Preprint), No. 940, 1976.

[3] C. Mauguin, *Compt. rend.*, 1928, **186**, 879; *Bull. Soc. Franc. Minér.*, 1928, **51**, 285.

[4] L. Pauling, *Proc. Nat. Acad. Sci., U.S.A.*, 1930, **16**, 123.

[5] H. Pezerat and J. Méring, *Compt. rend.* (*D*), 1967, **265**, 529.