Plasmon Spectroscopy as an Ultrasensitive Microchemical Tool

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A new microanalytical method, capable of rapidly identifying minute quantities (typically 10^{-14} g) of simple inorganic solids, is outlined and specific results for Al, Mg, MgO, and AlH_3 are described.

A collection of strongly interacting particles, such as the conduction electrons in a metal, can, under appropriate stimulation, sustain a charge density oscillation known as a plasma oscillation or plasmon. Plasmons may be observed in association with prominent peaks in the *X*-ray photoelectron spectra[1,2] and Auger electron spectra[3,4] of solids. Alternatively, when electrons are fired through thin films or scattered from the surfaces of suitable materials, plasmon peaks are observed in the energy loss spectrum at multiples of $\hbar\omega_p$ below the energy of the incident beam,[5-7] where ω_p is the frequency of the plasma oscillation. Inevitably, when materials are examined in an electron microscope plasmons are produced but these are only directly observable if, *inter alia*, an electron spectrometer is attached to the microscope. Using such an arrangement Egerton[8] has shown that plasmon peaks in electron energy loss spectra provide qualitative information about the nature of quasi-crystalline carbons.

In this paper we show that plasmon spectroscopy using an electron microscope provides a very sensitive and spatially highly refined microanalytical technique for identifying the nature of simple inorganic solids (metals, binary or ternary alloys, and compounds). This work arose during attempts to record K-edge and near-edge electron energy loss features of thin whiskers and fine powders of decomposed or partially decomposed metal hydrides (AlH_3 and MgH_2) full details of which constitute the subject of a separate report.[9]

In conventional transmission electron microscopy, small areas (*e.g.* less than 4×10^6 Å^2) of the specimen can be identified by selected area electron diffraction and occasionally by high resolution direct imaging.[10-12] For beam-sensitive materials, however, these two approaches, especially the latter, can prove futile because the specimen degrades in a time much shorter than that required to build up a satisfactory signal. This is true, in particular, for MgH_2 and AlH_3,

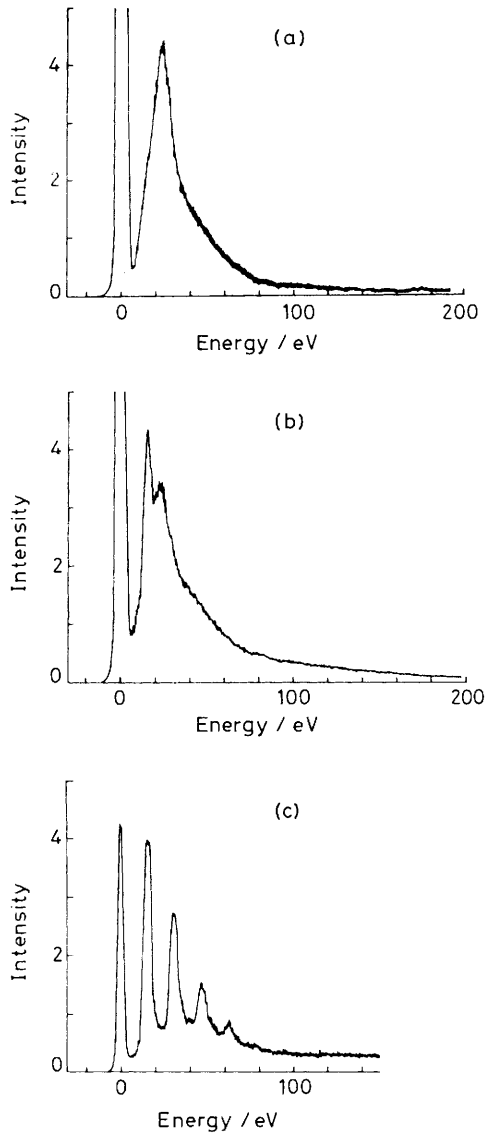

Figure 1. Plasmon peaks observed in the nominally AlH_3 sample: (a) is the spectrum observed immediately after inserting the specimen into the microscope and (b) and (c) the spectra after repeated exposure to the electron beam. The peaks in (c) are separated by 15.3 eV signifying that the final, irradiated state of the initial hydride is elemental aluminium.

discussed here. The intensities of the plasmon signals are, however, so large that, using standard commercial electron microscopes, accurate, quantitative data may be obtained from microscopic volumes of as little as 10^{-16} cm^3 on a time scale of seconds or so, which is less than that required to effect significant beam damage.

For a free electron Fermi gas executing simple harmonic oscillations the plasma frequency is given by equation (1),

$$\omega = [ne^2/m\epsilon]^{1/2} \quad (1)$$

where n is the electron density, m is the electron effective mass, and the other symbols have their usual meaning. For aluminium the calculated plasmon energy $\hbar\omega$ is 15.8 eV, and for magnesium 10.9 eV which compare well with the experimentally determined values of 15.0 eV for aluminium and 10.9 eV for magnesium.[6]

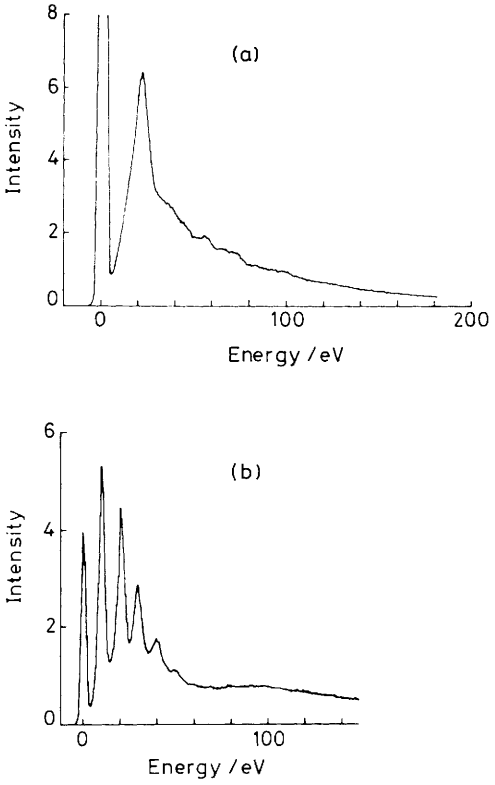

Figure 2. The plasmon spectra observed in the nominally MgH_2 sample: (a) is from the platelets and (b) is from the whiskers, and arise from MgO and Mg, respectively (see text).

Plasmon lines for simple metals are very narrow, the intrinsic line width being about 0.5 eV for both aluminium and magnesium.[6] However, if the particles are very small the line width increases up to 5 eV for 25 Å particles of aluminium.[13]

Very little data are available for the oxides of magnesium and aluminium and none is available for their hydrides. For Al_2O_3 the plasmon energy is reported to be 25 eV[4,14] and the full width at half maximum (F.W.H.M.) to be 20 eV. For MgO the peak is observed at 20 eV,[15] with a F.W.H.M. of 8 eV. Measurements were made on flakes or chips produced from freshly ground powders of AlH_3 and MgH_2 (prepared and handled as described elsewhere.[9,16]) Such measurements were carried out in a transmission electron microscope operating at 100 keV (with a vacuum of *ca.* 10^{-7} Torr), fitted with a magnetic prism spectrometer having a resolution of 4 eV.

Figure 1(a) shows the plasmon spectrum observed immediately after inserting platelets of 'AlH_3'. Figure 1(b) was recorded from the same area approximately 2 minutes later and Figure 1(c) after irradiating the specimen for about a further minute with a more focussed beam giving about 100 times the dose rate. The final state of the material is clearly seen from the plasmon harmonics (15.3 eV separation) to be pure aluminium. We rule out Al_2O_3 as the initial state from the absence of a K-edge signal for oxygen (at 530 eV), and we conclude that the single plasmon line at 23 eV (F.W.H.M. 18 eV) is typical of AlH_3 (see also ref. 16).

Filamentary samples taken from a specimen thought to be MgH_2 were found by plasmon microanalysis to be pure magnesium metal. The plasmon peaks are at 10.0 eV and harmonics thereof [Figure 2(b)]; moreover, their very narrow widths further confirm the metallic nature of the filaments.

In the spectrum of the flakes on the other hand there is a strong oxygen K-edge and the plasmon peak [Figure 2(a)], which remains unaltered after considerable electron beam irradiation, occurs at 22 eV (F.W.H.M. = 17 eV) signifying that the platelets are oxidic (MgO).

From the decay profile of the plasmon harmonics [Figure 1(c) and 2(a)] it is possible[17] to estimate the sample thicknesses. These turn out to be *ca.* 0.17 μm for aluminium and *ca.* 0.28 μm for magnesium.

In conclusion we note that both in respect to its sensitivity and ultimate discriminating power (the magnesium sample in Figure 2 is *ca.* 10^{-14} g), plasmon spectroscopy possesses exceptional promise. Using more powerful electron microscopes, in the scanning transmission mode for example, much smaller electron-beam probes can be employed, so that improvements in sensitivity of several orders of magnitude can be expected. In analogical terms the technique may be likened to identifying a bulk object by listening to the note emitted when it is struck by a hammer. Here, however, the volume of the object is typically 10^8—10^9 Å^3, and high energy electrons are used to set up their characteristic vibration. This technique is very well adapted to the identification of ultra-microcrystalline specimens of metals and binary compounds. With much less crystalline materials plasmon peaks become ill-defined[2,8] (the 'note' emitted by the struck object is less distinct) and, under these circumstances, it is more profitable to analyse the specimen by probing the momentum of the valence electrons. This can be done, also on a microscale, by means of Compton scattering, and a way of doing so is discussed in the following communication.[18]

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