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Valence Excitations in Electron Microscopy: Pursuing Zeitlerian Initiatives

A. Howie

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

Current exploitation of electron energy loss spectroscopy (EELS) in electron microscopy mainly focuses on the core state excitation region for losses $\Delta E > 200$eV. Characteristic edge signals suitable for microanalysis are readily available, the spatial resolution is usually limited only by electron optics and the theoretical tools are now well developed to extract useful additional electronic information from the structure of the excited state. Valence excitations on the other hand involve more spatially extended initial states, as indicated by the Bohr impact parameter $\eta v/\Delta E$, and the final states are potentially of collective (plasmon) as well as single electron type. Though relatively much more intense, these valence loss signals depend on the dielectric response and geometry of the nearby nanostructure and are therefore less simple to interpret. Nevertheless valence excitations are of increasing interest, not only to the burgeoning company of electron microscopists with GIF equipment, but also to wider communities in surface science, ceramics and biology. Fortunately the dielectric response theory of valence excitation by a fast electron has now been extended and tested for inhomogeneous nanostructures even in the relativistic regime. The way is open for many more quantitative studies of some of the salient problems as outlined below where, in addition to their seminal work on core excitations noted elsewhere in this symposium, Elmar Zeitler and his colleagues made several early and valuable contributions [1-6].

Surface plasmons and other valence excitations on small particles have recently attracted great attention in the context of near field optical microscopy [7] but can be generated and detected with much higher spatial resolution in electron microscopes. The influence of particle size, shape and surface coating have all been studied both in the context of the hydrodynamical model [1] as well as in the more general dielectric formalism [8]. Interactions of neighboring particles have also been observed [9]. A problem of great topical interest in apertureless near field microscopy is the local field enhancement effect experienced by a light wave incident obliquely on the region between the sample and the scanning tip[10]. Resonance with the tip-sample surface excitations can result in very large enhancement factors useful for highly localized spectroscopy, particularly when non-linear processes such as two-photon fluorescence spectroscopy or Raman spectroscopy are used [11,12]. The ultimate usefulness of this form of highly localized spectroscopy will depend on more complete study of the dependence of the field enhancement factor on the tip shape and dielectric coupling between tip and sample. Robust operating conditions that can routinely be achieved will be essential.

The dielectric response of a body also can be used to evaluate the image force experienced by a passing fast electron [2]. Similarly the Casimir or van der Waals forces between two or more dielectric bodies depend on their dielectric response functions and can be computed (including retardation effects if necessary) for any given geometry [13]. These forces are generally, though not always attractive, and are for instance involved in determining the thickness of intergranular layers in ceramics [14]. Transmission electron microscopy is obviously in a unique position to tackle such problems since, at the same time as the structure is imaged, the relevant dielectric functions of the various regions can be determined from the localized valence loss spectra. The

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variations in the valence loss spectra near interfaces in materials and from point to point in biological samples [15] may in any case be large enough to yield analytical information which can usefully supplement the core loss spectral data, particularly in samples susceptible to beam damage.

Ionisation damage places severe limitations on the more widespread application of high resolution electron microscopy despite the successful development of sophisticated cryomicroscopy and minimal dose techniques [3]. The final stage of electronic excitation leading to irreversible atomic displacement is usually some form of valence excitation, either through a direct valence loss event leaving a single hole in the valence band or through an initial core loss event followed by an Auger decay leaving two holes in the valence band. In aliphatic organic molecular crystals such as paraffin where high resolution imaging is achieved only with great difficulty [4], the former process appears to operate. Core excitation leading to Auger decay has been identified as the key process in many oxides [16] and possibly also in aromatic organic crystals [17]. The very low electron energies, such as those employed for PEEM imaging of surface processes [5,18], may sometimes lie below the damage threshold energy for all the above processes so that a damage-free energy window may exist. Exciton capture sometimes provides yet another damage process at these low energies [19] but is a resonant process with a sharply defined energy and may also be avoidable. In clarifying our picture of these phenomena new experiments, particularly comparison of photon and electron desorption cross sections and energy thresholds in different materials would be very valuable. In the valence excitation region, the two cross sections can differ not only because of momentum transfer effects [6] but also because of valence electron screening [20].

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