

## Band structure of solid inert gases

from B. L. Smith

THE inert gases have long been recognised as useful tools with which to develop the atomic theory of solids, liquids and gases. In the past twenty-five years much progress has been made, but there still remain considerable gaps in our understanding of these 'simple' systems.

In principle, properties of the solidified inert gases, including both thermodynamic and optical behaviour, can be determined by solving the Schrodinger equation, using the total Hamiltonian for all ions and electrons within the solid and their mutual interactions. In practice, the many body problem has to be reduced to manageable proportions by using approximations appropriate to the physical property under consideration. Thus virtually all the different approaches to the problem lead to essentially the one-electron approximation, that is, the band-structure formulation of the electron states, or to the exciton picture of excitations within the solid. A large number of band-structure calculations have now been carried out for the solidified inert gases.

The theoretical predictions can be compared with experimental data by measuring the reflectivity, absorption coefficient and the energy loss function. These, together with more recent determinations of photoemission, allow gap energies and electron affinities to be estimated. Accurate measurements are however extremely difficult because of various technical difficulties encountered in the experiments.

Photoelectron energy distribution curves for the solidified inert gases have recently been determined by N. Schwenter and coworkers at the University of Munich, in collaboration with E. E. Koch of the Deutsches Elektronen Synchrotron (DESY), at Hamburg (*Phys. Rev. Lett.*, **34**, 528; 1975). These measurements represent the first comprehensive set of experimental data for the actual band structure. They are important because they provide direct information concerning the structure of the valence bands, the influence of the conduction bands on the photoelectron energy distribution curves, and some details of electron-electron scattering processes. In particular, the data highlight the discrepancies which exist between the results of various band-structure calculations which have recently been reported.

Measurements were made on films of solid neon, argon, krypton and xenon, 20–100 Å thick, using the DESY synchrotron as a broad-band vacuum

ultraviolet light source. The excitation energy was varied continuously between 8 and 30 eV with a typical resolution of 200 meV. Because the films were very thin, charging of the samples—one of the major problems encountered when investigating photoemission of insulators—was kept to a minimum.

The results provide a wealth of information about the band structure. In the first place, the vacuum level  $E_V$  is obtained directly and unambiguously for each solid. These values, combined with data for the gap energies  $E_G$  determined from absorption and reflection measurements, allow the electron affinities  $E_A = E_V - E_G$  to be estimated and compared with the results of earlier photoelectron yield determinations. For example,  $E_A$  for neon is found to be both large and negative (–1.4 eV), which confirms the negative value predicted theoretically, and is consistent with the trend observed experimentally for the other inert gases.

Above threshold, the width of each energy distribution curve increases with increasing photon energy until the photon energy is sufficient to excite electrons from the bottom of the valence band. In this region the width of the curve corresponds to the width of the valence band and is independent of the energy of the exciting photons. Photoemission thus allows the valence band width to be estimated. Schwenter found that the widths of the energy distribution curve increased systematically from neon to xenon as might be expected from the spin-orbit splitting, and were larger than the widths predicted by most band-structure calculations.

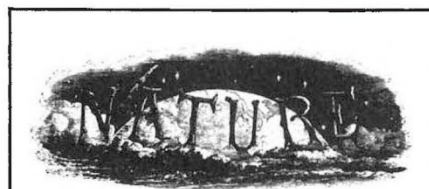
There are some interesting anomalies which arise when examining the various band-structure calculations. For example, relativistic calculations for krypton result in a total band width that is 0.5 eV smaller than that observed (2.3 eV), whereas non-

relativistic calculations exceed the experimental width by similar amounts. The best agreement between theory and experiment is obtained by simply adding the spin-orbit energy to the width of non-relativistic bands obtained by Kunz and Mickish (*Phys. Rev.*, **B8**, 779; 1973), but this procedure is somewhat dubious.

Three maxima are noted in typical photoelectron energy distribution curves for xenon but these are not detected for the other solidified inert gases, presumably because of the overlapping caused by the smaller spin-orbit splitting and smaller total band width in the other solids. The shape and relative intensities of the curves are found to depend strongly on the exciting photon energies. Using the experimentally determined parameters for the valence bands, these variations can be used to obtain estimates for the structure of the density of states in the conduction bands. For example, the first maximum of the density of states can be deduced, which corresponds to flat regions of the lowest conduction band. The experimental data thus yield new and important information about the structure of the conduction bands, hitherto unobtainable by other methods.

How do the above calculations and measurements relate to the cohesive energy in the solidified inert gases? It is known that one-electron energies, as obtained for example from Hartree-Fock calculations, over-emphasise Coulomb and exchange terms. More importantly, band energies do not fully include electron-electron interactions. Since electron-electron correlations would be expected to be important in the case of the inert gases, these calculations need some modification to take these effects into account. For example, the basic Hartree-Fock assumption that the ground state wave function can be described as a single Slater determinant of one-particle wave functions can be modified by including excited one-particle wave functions in the combination. But this and other approaches soon run into computational difficulties and still no entirely satisfactory method exists for solving the problem.

Eisenschitz and London carried out the perturbation calculation in 1930 which established the attractive part of the force between two non-polar atoms—the Van der Waals or dispersive term. In the following decade it was confidently predicted that because the atomic polarisability had been linked to interatomic forces, once the structures of the solidified inert gases were established, it would be a relatively simple matter to relate the atomic properties to the bulk thermal and mechanical behaviour.



### A hundred years ago

THE preparations for the Geographical Congress in Paris are being actively completed. The large map of France executed by the staff officers will be exhibited, all the sheets having been joined, thus forming one continuous sheet of paper of immense size. The map will be exhibited at the Tuileries in the Salle des États. It will be photographed by the microscopical and panoramic process.

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