100 YEARS AGO

The possessors of certain hereditary characters are unquestionably *sub-prolific*; that is, they eventually contribute less than their average share to the stock of the future population. It may be that they die before the age of marriage, or that they are sexually unattractive or unattracted, or that if married they are comparatively infertile, or that if married and fertile the children are too weakly to live and become parents. It is very probable, though I have no trustworthy facts to confirm the belief, that persons affected with hereditary insanity are sub-prolific because their families, if they have any, are apt to contain members who are afflicted in various ways that render them less likely than others to live and to marry. But I do not propose to go into the details of this or of any other malady, but merely mention it as an illustration of what is meant, when I assume that the possessors of some particular characteristic, not necessarily a morbid one, and which may be called A, are sub-prolific on the average.

From *Nature* 11 May 1899.

50 YEARS AGO

Reports of tumours in insects are relatively rare. Paillot mentions proliferation in the fat cells of *Euxoa segetum* Schiff., following infection by virus diseases (pseudo-grasseries I and II). Tumours have been described in the fruit-fly, *Drosophila melanogaster* Meigen, by Stark and Russell: in larvae of the Pygaera group of butterflies, by Federley; and in the stick insect, *Dixippus morosus* Br., by Pflugfelder. They have been found in a large Orthopteran insect, *Leucophaea maderae* F., by Scharrer. All the tumours so far discovered in insects are apparently non-malignant, although malignancy has been claimed by Stark and Federley. Russell found that those in *Drosophila* reported by Stark as malignant were similar in structure to benign tumours occurring in the same insect, and that the so-called malignant tumours could be successively transplanted without hampering the development of the host. The tumour strains discovered by Federley apparently have been lost. Various stimuli will provoke tumour proliferations in insects. Spontaneous tumours occur in several genetic tumour strains in the fruit-fly, but the stimulus is not known.

From *Nature* 14 May 1949.

calmodulin, can both inactivate and facilitate Ca^{2+} channels. □

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Materials science

The hard problem of carbonitrides

Barry M. Klein

'Materials by design' is the goal of theorists who are developing a fundamental understanding of the macroscopic properties of materials from a microscopic, atomistic point of view. In a paper on page 132 of this issue, Jhi *et al.*[1] move us towards this goal by relating the hardness properties of carbonitrides — compounds containing carbon or nitrogen, together with a transition metal[2] — to fundamental aspects of the material's electronic structure such as the electronic energy bands, or the charge density and chemical bonding. They show that the elastic properties of the carbonitrides, which relate to their hardness, can be explained by the filling of electron states depending on whether the underlying lattice is occupied by transition-metal or carbon and nitrogen atoms, or by vacancies. The authors have used state-of-the-art theoretical and computational methods to reach this conclusion from first principles, without recourse to tweaking the theoretical parameters with experimental data. An understanding of the hardness of the carbonitrides does not seem so hard any longer.

Carbonitrides (such as TiC or NbN) often form in the simple NaCl crystal-lattice structure of ordinary table salt. The valence electron concentration, or number of electrons that are active in the bonding of these materials (there are eight such electrons in TiC, and ten in NbN) can be changed by forming alloy compounds with varying amounts of transition metal(s), carbon and nitrogen atoms, or vacancies. Such materials often have interesting properties ranging from superconductivity at relatively high temperatures[3,4] (for example, T_c > 17 K for NbN), to high melting temperatures, and to the extreme hardness (such as TiC, which has a relative hardness somewhere between that of aluminium oxide and diamond) that makes them important materials for cutting tools and related applications.

Hardness is defined empirically as resistance of a material to denting or scratching. Relative hardness may be determined by a material's response to an 'indenter' pressed into, or moved along, its surface. The hardness and related mechanical properties of materials often involve complicated phenomena such as the motion or pinning of dislocations (mismatched lattice planes), or other 'large defect' properties of solids that, ultimately, should relate back to the fundamental microscopic properties of the perfect lattice. Theoreticians have long nibbled away at the problem of relating the hardness of carbonitrides to the underlying chemical bonding that is governed by the electron distribution in these materials. But unravelling the underlying properties of carbonitrides in terms of quantifiable physical and chemical quantities such as 'bonding' has been limited to qualitative descriptions of these materials, such as describing them as 'covalent metals', in analogy to hard semiconductor materials such as diamond.

It is only in the past decade that theoreticians have been able to study electronic structures with enough accuracy to be able to determine fundamental properties such as elastic behaviour and lattice-vibrational properties of solids from first principles. Using the formalism developed by Walter Kohn and colleagues (see for example, ref. 5) that led to his share of the 1998 Nobel Prize in Chemistry, an elaborate but computationally workable machinery for doing quantitative studies of the electronic structure of materials has become possible (see ref. 6 and references therein). In essence, the resulting so-called Kohn–Sham equations reduce the solid-state many-body problem (roughly 10^{23} electrons and nuclei for each cubic centimetre of a solid) to a set of one-particle Schrödinger equations that need only be solved in a single unit cell of a perfect, periodically repeating solid. The results for properties of solids in the ground state

— such as structural features (bond lengths), elastic behaviour and lattice vibration frequencies — has in many cases agreed with experiment to within a few per cent. The only experimental input into these calculations is an assumed crystal structure, but even the ground-state crystal structure can be determined by these methods using a total-energy-minimum search procedure[7].

The observed maximum in hardness of carbonitrides occurs for a non-integral value of the valence electron concentration, corresponding to major deviations from the properly occupied NaCl lattice structure. In general, such a loss of lattice periodicity would render accurate theoretical calculations impossible. However, one of the remarkable properties of the carbonitrides is their 'rigid band' behaviour, whereby the varying valence electron concentration (alloying) can, to a very good approximation, be modelled by simple changes to the perfect lattice calculations. This rigid-band-like behaviour is one of the reasons that the work by Jhi *et al.*[1] was possible.

What Jhi *et al.* have shown is that there is a correlation between the behaviour of the elastic constants and, by implication, the hardness, with the filling of electron-bonding states formed by the carbon and nitrogen *p*-electrons and the transition-metal *d*-electrons. In greater detail, there is competition between the filling of a set of states favourable for elastic strength and a set of states having the opposite effect. This competition results in a maximum in elastic constants such as the shear modulus — which measures the ability of a material to recover from transverse stress — as a function of electron filling, in direct correlation with a similar maximum for the hardness that has been observed in experiments. In particular, Jhi *et al.* find that the maximum in the shear modulus occurs for a valence electron concentration corresponding to a carbon or nitrogen vacancy concentration of 12%, in agreement with material testing.

Particularly interesting is that the bulk modulus of the carbonitrides, which is determined by a homogeneous volume deformation of the crystal, does not show any maximum as a function of valence electron concentration. The authors point out that as much as we like to think of the carbonitrides, with respect to their covalent-like charge density and bonding, as being analogous to covalent semiconductors, there are differences. In semiconductor or insulator alloys the hardness and the bulk and shear moduli vary in the same way with electron concentration. But the existence of two different types of energy bands for the least tightly held electrons in carbonitrides leads to different responses to shear and volume deformations.

Materials theorists are making huge progress in relating macroscopic properties of materials to the fundamental atomic constituents of matter. Both the complexity and the understanding revealed by studies such as that by Jhi *et al.*[1] illustrate that, along the road to 'materials by design', we can anticipate traversing some interesting terrain. □

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Photosynthesis

Mixed metabolism in plant pools

Peter D. Moore

Assemblages of plants present ecologists with some interesting conceptual problems. How can a number of species coexist when they are tapping the same set of environmental resources? All require light energy, plus a source of atmospheric (or dissolved) carbon, together with water and a fairly standard range of elements for their growth and development. So, cohabitation must depend on the plants' capacity to tap these resources in different ways, coupled with their ability to cope with the stresses that any particular habitat may present. Although such issues have been studied in terrestrial habitats, aquatic ecosystems — particularly ephemeral (or transient) aquatic habitats — have been neglected. But Jon Keeley of the United States Geological Survey Biological Resources Division in California has begun to redress the balance. Reporting in *Functional Ecology*[1], he describes his latest findings on the various photosynthetic processes found in the vegetation of temporary pools.

Keeley has looked at the photosynthetic ecology of shallow pools for many years. In 1981, he discovered a quillwort, *Isoetes howellii*, a small aquatic pteridophyte which, unexpectedly, showed the characteristics of crassulacean acid metabolism (CAM)[2]. This photosynthetic system involves the accumulation of carbon using the enzyme phosphoenolpyruvate carboxylase as the initial stage in the fixation process, rather than the more usual ribulose 1,5-bisphosphate carboxylase–oxygenase (which results in the formation of 3-carbon products, leading to the term C_3 plants for those that use this system; Fig. 1). Crassulacean acid metabolism is most frequently associated with arid, terrestrial conditions — the short-term storage of fixed carbon in the form of organic acids allows plants to accumulate carbon during the night, enabling them to conserve water by keeping their stomata (the pores through which they take in CO_2 and, consequently, lose water) closed during the day.

The potential advantage of CAM for an

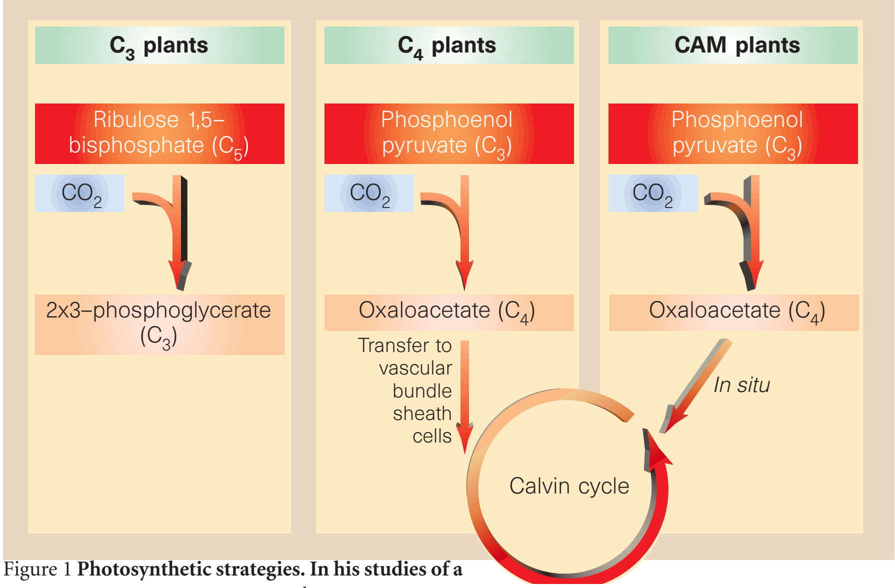

Figure 1 **Photosynthetic strategies. In his studies of a transient shallow pool, Jon Keeley[1] has found that aquatic plants use a variety of photosynthetic strategies, allowing them to coexist and make best use of the available resources.**