SOLID STATE CHEMISTRY

Metastable Dense Semiconductor Phases

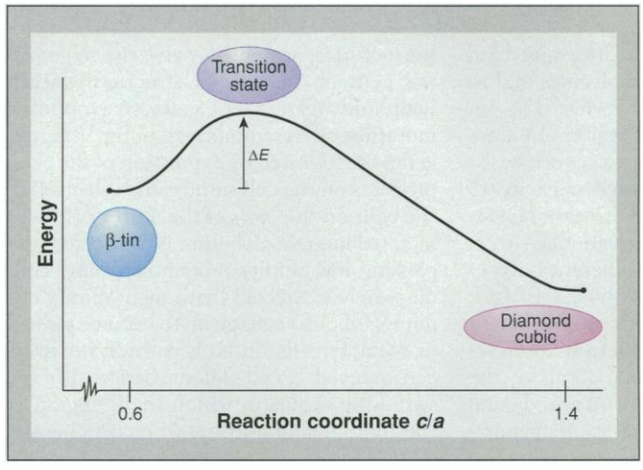
Louis Brus

Materials scientists seek to understand how to create new substances. One strategy is to explore thermodynamic metastability, that is, to search for materials seemingly unfavored by their higher energy, yet permitted to exist by barriers that prevent a transformation to lower energy forms. On page 398 of this issue, Chen *et al.* (*1*) report direct studies of solid-solid structural phase transitions in cadmium selenide nanocrystals. These results suggest that crystalline high-pressure phases may be generally metastable at normal (standard) pressure and temperature (STP).

The story of C_{60} demonstrates the importance of kinetics and synthesis in solid materials. At room temperature and pressure, the C_{60} phase energetically lies about 0.45 electron volt per carbon atom above the diamond and thermodynamically stable graphite phases of carbon. Yet, C_{60} is perfectly stable at STP, as was intuitively clear when the beautiful closed-shell molecular structure was first postulated in molecular beam studies (*2*). Belief in the stability of this structure motivated an enormous search over 5 years for a practical synthesis. An utterly unexpected, high-yield aerosol method was found (*3*), which led in turn to the discovery of carbon nanotubes in arc electrodes (*4*).

Diamond, graphite, and the fullerenes are each stable at STP because the chemical bonding is strong, directional in space, and so different in each phase. These features create huge kinetic barriers to bond deformation along any direct pathway from one phase to another. The C_{60} aerosol synthesis only succeeds by essentially creating free gas-phase carbon atoms, at enormous temperature and energy cost, and then reassembling them. There are other examples of metastable phases. In quartz, silicon is sp^3 hybridized. At high pressure there are other phases, including stishovite, in which silicon has octahedral coordination with six oxygen nearest neighbors (*5*). Stishovite has a density about 60% higher and a refractive index 30% higher than those of quartz. Once made, stishovite is perfectly stable at STP; 100-μm single crystals have been recovered from high-pressure anvil experiments. Think what might be possible if we could make stishovite as easily as amorphous silica or quartz.

Like silica, the semiconductors InP, GaAs, GaN, ZnSe, Ge, and Si all exhibit tetrahedral sp^3 bonding in their thermodynamically stable phases at STP. They also have a series of denser high-pressure phases, in which they are electrically either semiconductors of smaller band gap or metals. For example, GaAs undergoes a transition from zinc blende to the six-coordinate rock-salt form near 5 GPa, with a theoretical volume contraction of 17% (*6*). As the transition occurs, a 50-μm single crystal irreversibly fragments into 5-nm rock-salt domains. The structure and physical properties change gradually with increasing pressure because of internal strain from the incipient volume change, unlike what would be expected for an ideal first-order phase transition. The kinetics are poorly understood.



Pathway along the transition from a nearly round silicon nanocrystal with β-tin structure to one with the prolate diamond-lattice structure. The energy of the structure is plotted against its crystallographic *c/a* ratio. The high-activation barrier ΔE stabilizes the β-tin form.

Size may be a key experimental variable in these questions of mechanism, metastability, and facile synthesis. Alivisatos and co-workers have studied the pressure-induced four- to six-coordinate transformation (wurtzite to rock salt) in small CdS cluster molecules, 2- to 6-nm CdSe nanocrystals, and 20- to 50-nm diamond-lattice Si nanocrystals (*7*). Unlike in the 50-μm "bulk" GaAs studies, they find just one nucleation event per nanocrystal; a single crystallite of one phase reversibly transforms into a single crystallite of the other phase. The entire nanocrystal changes shape as well as volume to accommodate the underlying unit cell shape and volume change. In large Si nanocrystals, this shape change has been confirmed by x-ray diffraction at high pressure.

Chen *et al.* now report the first time-resolved direct kinetic studies of this process, using defect-free CdSe nanocrystals (*1*). Simple unimolecular first-order kinetics occur on a time scale of minutes to hours, after a pressure jump. The conversion rate is slower for larger nanocrystals; the activation energy scales nearly linearly with the number of unit cells. This variation is the signature of a coherent process, like molecular isomerization, in which all unit cells simultaneously fluctuate from one phase to the other. The entire nanocrystal is the critical nucleus.

This coherent fluctuation mechanism was recently proposed and modeled for the Si nanocrystal transition from six-coordinate β-tin to the four-coordinate diamond phase (*8*). Nanocrystal shape is very important because of the large change in crystallographic *c/a* ratio from 0.55 in β-tin to 1.414 in diamond (see figure). To accommodate this distortion, a compact β-tin nanocrystal becomes a strongly prolate diamond-lattice nanocrystal of high surface area. This increase in surface area contributes to a relatively high-activation barrier and a half-life of many years for β-tin nanocrystals > 2 nm.

The larger a six-coordinate nanocrystal, the more metastable it is against reversion to the four-coordinate state. Chen *et al.* propose that there is a practical optimal size for metastability: the largest size at which the nanocrystal can be prepared defect-free. In the related and better understood solid-solid phase transformations of martensitic metals, nucleation is thought to be always catalyzed by extended structural defects (*9*), which may be the case in semiconductors as well. How then can single crystals of the high-pressure phases be made? Although it is possible at a pressure of several

The author is in the Department of Chemistry, Columbia University, New York, NY 10027, USA. E-mail: brus@chem.columbia.edu

gigapascals, it is hard to prevent reversion upon return to STP because of the strain generated during pressure release. Exceptions exist: stishovite SiO_2 (as mentioned), ZnO (*10*), and AlN (*11*).

In normal processing, synthesis occurs directly from the elements or free atoms, and the temperature is high enough to convert amorphous material to crystalline material. The thermodynamic phase is invariably obtained. Perhaps instead one could catalyze synthesis of metastable phases under milder conditions closer to STP. Catalysis, well developed in organic synthesis and biology, remains primitive in solid materials. Catalysis may be involved in two recently reported reactions: GaN nanocrystals with the rocksalt structure have been made in benzene solvent at 280°C and a pressure of about 50 bar, conditions far below the region of rocksalt thermodynamic stability (*12*). Also, rocksalt CdS has been reported in a reaction templated on a polyethylene oxide film (*13*). The mechanisms are not known. In a manner similar to C_{60}, perhaps belief in the metastability of the six-coordinate phases will encourage discovery of novel and practical reactions, and thus a new area of semiconductor materials.

References

1. C.-C. Chen, A. B. Herhold, C. S. Johnson, A. P. Alivisatos, *Science* **276**, 398 (1997).
2. H. Kroto, J. Heath, S. O'Brien, R. Curl, R. Smalley, *Nature* **318**, 162 (1985).
3. W. Krätschmer, L. Lamb, K. Fostiropoulos, D. Huffman, *ibid.* **347**, 354 (1990).
4. S. Iijima, *ibid.* **354**, 56 (1991).
5. S. Stishov and S. Popova, *Geochemistry* **10**, 923 (1961); L. Lin, W. Bassett, T. Takahaski, *J. Geophys. Res.* **79**, 1161 (1974).
6. J. Besson *et al.*, *Phys. Rev. B* **44**, 4214 (1991).
7. S. H. Tolbert and A. P. Alivisatos, *Science* **265**, 373 (1994), and references therein; *Chem. Phys.* **102**, 1 (1995); S. Tolbert, A. Herhold, C. Johnson, A. P. Alivisatos, *Phys. Rev. Lett.* **73**, 3166 (1994); S. Tolbert and A. P. Alivisatos, *Annu. Rev. Phys. Chem.* **46**, 595 (1995); S. H. Tolbert, A. B. Herhold, L. E. Brus, A. P. Alivisatos, *Phys. Rev. Lett.* **76**, 4384 (1996).
8. L. Brus, J. Harkless, F. Stillinger, *J. Am. Chem. Soc.* **118**, 4834 (1996).
9. G. Olson and M. Cohen, in *Dislocations in Solids*, F. Narbarro, Ed. (North-Holland, Amsterdam, 1986), vol. 7, chap. 7.
10. C. H. Bates, W. B. White, R. Roy; *Science* **137**, 993 (1962).
11. H. Vollstadt, E. Ito, M. Akaishi, S. Akimoto, O. Fukunaga, *Proc. Jpn. Acad. Ser. B* **66**, 7 (1990); I. Gorczyca *et al.*, *Solid State Commun.* **79**, 1033 (1991); Q. Xia, H. Xia, A. J. Ruoff, *Appl. Phys.* **73**, 8198 (1993).
12. Y. Xie, Y. Qian, W. Wang, S. Zhang, Y. Zhang, *Science* **272**, 1926 (1996).
13. J. Lin, E. Cates, P. A. Bianconi, *J. Am. Chem. Soc.* **116**, 4738 (1994).

IMMUNOLOGY

Antigen Presentation by Memory B Cells: The Sting Is in the Tail

David Tarlinton

Immunoglobulins, or antibodies, must bind to a vast array of foreign molecules and so themselves exist in many forms. The sequence in the variable (V) region of immunoglobulin molecules varies enormously, conferring virtually unlimited capacity to bind antigen. The so-called constant (C) region comes in five different varieties—α, δ, ε, γ, and μ—providing five different isotypes [immunoglobulin A (IgA), IgD, IgE, IgG, and IgM], each of which performs a different suite of functions. Finally, there are both secreted and membrane-bound forms of the immunoglobulins. The membrane-bound immunoglobulins are critical in the generation of B cell–mediated immune responses, participating in both signal transduction and antigen processing. Now, three sets of experiments reported on pages 407, 409, and 412 of this issue (*1–3*) and one soon to appear in *EMBO Journal* (*4*) present new information on how the many membrane-bound forms of immunoglobulin control B cell function.

Upon activation by antigen, B cells follow one of two differentiation pathways: They may differentiate directly into plasma cells, which are basically antibody-secreting factories, or they may give rise to germinal centers, specialized structures within lymphoid organs. Here, successive rounds of mutation of the immunoglobulin V region genes are followed by expression of the gene products on the cell surface and selection of the cells on the basis of the affinity of these mutated immunoglobulins. Nonselected (expressing low-affinity immunoglobulin) cells die, whereas selected (with high-affinity immunoglobulin) cells go on to become plasma or memory cells. In both pathways of antigen-induced B cell differentiation, isotype switching occurs in which the C region of the immunoglobulin heavy chain changes from the joint expression of IgM and IgD on naïve B cells to expression of one of the downstream isotypes: IgG, IgA, or IgE.

> An enhanced version of this Perspective with links to additional resources is available for *Science* Online subscribers at http://www.sciencemag.org/

Throughout the differentiation process, the surface-bound immunoglobulin must perform two functions: signal transduction and the transport of captured antigen to an endosomal compartment for processing and presentation on the cell surface in association with major histocompatibility complex class II. But how are these dual requirements to be fulfilled in the face of the changing character of the immunoglobulin molecule, as the joint expression of IgM and IgD isotypes on naïve B cells changes to IgA, IgG, or IgE isotypes on the mature B cell?

The answer to this question at first appeared to be quite straightforward. In order to be expressed on the B cell surface, most immunoglobulins must be associated with two other polypeptides, Ig-α and Ig-β (see the figure) (*5, 6*). Both Ig-α and Ig-β contain a sequence (called ITAM) that can cause activation of protein tyrosine kinases, such as Syk and Lyn, accounting for the ability of isotype-switched B cells to signal in response to antigen (*7*). In addition, the cytoplasmic tails of Ig-α and Ig-β are sufficient for the internalization of surface proteins and their targeting to endosomal compartments for processing (*8*). It had been assumed, therefore, that both signaling and antigen-processing functions served by transmembrane immunoglobulins would be dependent on these unchanging accessory polypeptides. But the new results in this issue and elsewhere (*1–4*) show that the situation is far from being this simple and is therefore certain to be of even greater interest.

In these experiments, the cytoplasmic tails of the IgGs and IgE have been manipulated. Mouse and human IgM and IgD have a three–amino acid tail (Lys-Val-Lys), that of IgA has an additional 11 amino acids, and those of the IgGs and IgE are extended by 25 amino acids (*6*). The cytoplasmic tails of the IgG subclasses have many amino acids in common with each other and somewhat fewer in common with IgE.

The function of the conserved portion of the IgG2a cytoplasmic tail was investigated by Weiser *et al.* by using site-directed mu-

The author is at The Walter and Eliza Hall Institute of Medical Research, Post Office Royal Melbourne Hospital, Victoria 3050, Australia. E-mail: tarlinton@wehi.edu.au