

NEW MATERIALS: FOUNTAINHEAD FOR NEW TECHNOLOGIES AND NEW SCIENCE

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Abstract

The role of materials as the benchmark technologies which give epochs of human history their names continues into the present. The discovery of new materials has nearly always been the source of new materials science, and frequently of new technologies.

This paper analyzes the actual processes by which new materials are synthesized, i.e. whether driven by serendipitous observations, new knowledge pulled by the market, or integrated into a technological thrust. This analysis focuses on modern ceramic materials discoveries, since WW II, and uses 45 years experience in materials synthesis in the author's own laboratory as case studies.

A dozen different families of materials or processes are involved: hydrothermal reactions; sol-gel processing; clays and zeolites; electroceramics; zero expansion ceramics; diamond films; radioactive waste host phases. Nanocomposite concepts introduced by the author a decade ago offer an entire, large, new class of materials which will dominate synthesis for the next period.

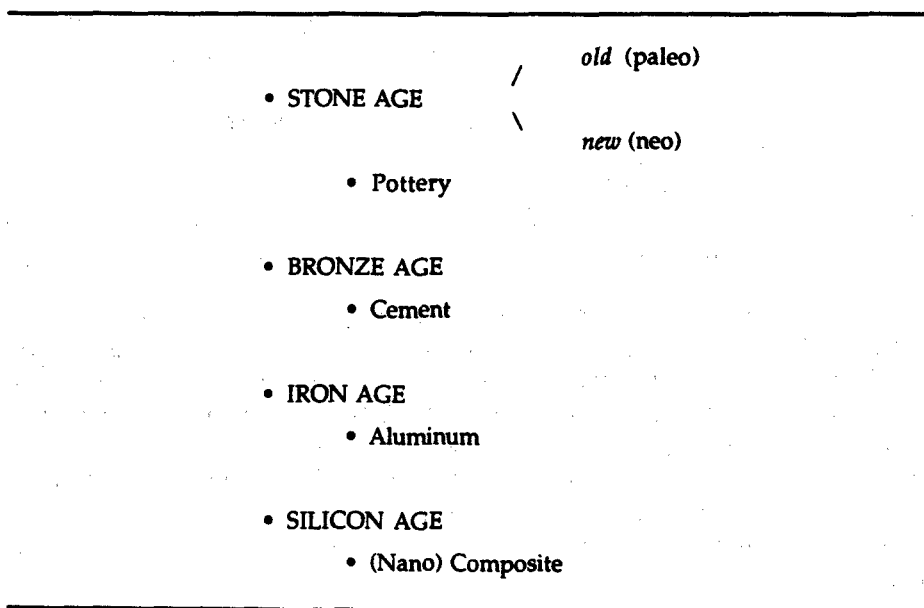
The future of materials research for the next 25 years cannot be extrapolated from the past 25 years. We are near the asymptote for materials utilization in most metals. Likewise we are approaching saturation in improvement of many useful properties. Justifying much further "basic" R/D for incremental improvement in civilian-oriented industries will not be easy. In materials synthesis the near-term future is sure to emphasize not "new phases," but tailored micro- and nano-composites for chemical, electrical, optical and magnetic uses. Unexpected new discoveries such as the Lanxide process may offer the rarer chances for step function advances.

The new structure of knowledge management will rely less on local research than on integration of worldwide inputs. Better scientific and technological opportunities will lie in designing knowledge intensive materials to meet the new environmental and conservation goals, and the human needs of the very large numbers at the bottom of the socio-economic structures of the world.

THE ROLE OF MATERIALS IN HUMAN SOCIETY

This rather bold title has been chosen to call attention to the long-neglected pivotal role that the discovery of a new material or a new process for making—typically new—materials has played in the progress of humankind and its the science of materials.

Figure 1 recalls that historical epochs have been named after materials. Today our post WW II epoch would be accurately named as the silicon era. We will conclude this paper by claiming that the next era will be that of the nanocomposites. Figure 2 brings together some characteristics of all the materials that humankind uses. In national and world policy it is important to have a feel for the volumes of the different materials actually used. Many are surprised to find the rank order of the tonnages of these materials: wood; ceramics including cement; metals; polymers; and semiconductors. Another interesting comparison in Figure 3 introduces the importance of the comparative scale in very



"FIDES SUBSTANTIA RES" Teilhard de Chardin

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Figure 1. The "progress" of human history has been marked by (new) materials. It is not an unreasonable index as the philosopher scientist Chardin observed "Faith is the substance of things." I have paraphrased the modern situation for many societies on the right, is "Materials give substance to hope."

	Use Started In	Millions of Tons/Year	Resources Needed	Products	Properties Utilized
WOOD (natural composites)	3,000,000 B.C.	1-10,000	renewable, but somewhat geographically limited	building	mechanical
CERAMICS Incl. <u>cement</u>	<10,000 B.C.	1-10,000 1,000	SiO ₂ , Al ₂ O ₃ , CaO, MgO Fe ₂ O ₃ <u>universally available</u> no resource problem for any nation	pottery glass - bulk - optical cement; refractories; cutting tools; diamonds; turbines	mechanical optical electrical
METALS	5,000 B.C.	iron = 500 others = <500	viable ores geographically very uneven	myriad products steel, copper, aluminum alloys	mechanical electrical
SEMICONDUCTORS	1940	<<.001	no resource issue	small electrical devices	electrical
POLYMERS	1900	~100+	petroleum (now)	containers, furniture, textiles	mechanical (electrical)
COMPOSITES	1950	1-10	not important	furniture to airplanes	mechanical (electrical)

Figure 2. The Material World.

Factor	Highway Materials Asphalt & Concrete	Superalloy	Microchip	Ceramic Matrix Composite
Tons/yr	1,000,000,000	50,000	100	10
Second phase	Stone, rebar, pores	γ'	Epitax layer	SiC
Size of second phase (nm)	From 1 up to 10^{10}	10^3	10^2	10^4
Cost, \$/#	0.05	100	23,000	100
U.S. Research Effort	3×10^7 (1977)	10^8	10^{9+}	10^8

Figure 3. The enormous range in contemporary materials (after R. Decker), in volume, size, price, and total research effort which is not related to the business opportunity.

different parameters among different materials. Not only volumes and size and second phase are significant. One notes that the research effort bears some relation to the cost per pound, but none at all to the total volume of cost of the class of material. Figure 4 is a summary of the status of our ability today to design to specification and synthesize materials, by the size of the units involved in composite or single phases. The larger the size from meters to tens of micrometers, the more advanced our ability. At the unit cell or "atomic" level our synthesis ability is still very primitive indeed. It is a major thesis of this paper that the nanocomposite level provides the level of aggregation which will form the frontier for materials research worldwide in the immediate future.

<u>Macro</u> (cm-m)	Excellent	Materials for very large structures have been optimized; e.g. reinforced concrete, airframe alloys.
<u>Micro</u> (mm- μ m)	Very good	Lab scale and small objects (GRP to graphite-epoxy composites; transparent Lucalox, composite transducers, etc.).
<u>Nano</u> (0.1 to 10 nm)	Primitive but new	New materials <i>designed</i> and made: intercalates, glass-ceramics, toughened zirconia, nanocomposite desiccants, etc.
<u>Atomic</u> (0.1 nm)	Poor	New materials found by serendipity: penicillin, teflon, magnetic garnets, R.I.B., 1:2:3 superconductors, etc.

Figure 4. A comparison of our contemporary capacity to prepare new materials or composites arranged as a hierarchy of size.

THE INNOVATION PROCESS

We turn now to the question of what the historical record teaches us on how innovation has occurred in science and technology.

In earlier reviews (1,2) I have referred to the work of J. D. de Solla Price (3), one of the great historians of science who shows definitively how much advances in all branches of sciences depended on new instruments. I argued by analogy (4) that “new materials” play exactly the analogous role in the materials sciences and technologies. The relationship is that shown in Figure 5. This figure makes several points. First it supports Price’s contention (the title of his AAAS address) that by and large (contrary to the totally unsupported maxims of many scientists in academia), *science is largely applied technology*. From Galileo, applier of the telescope, to the modern particle accelerators appliers of magnet and electronic technology, there is no room for argument that in most cases, as Price puts it, “the

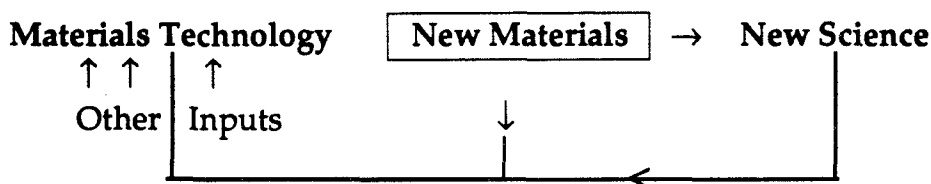


Figure 5. In parallel with de Solla Price’s assigning of the key role to new instruments in advancing science and then technology; new materials can independently advance both materials science and materials technology. The science has not led to new materials, except increasingly in the design of composites.

arrow of causality” is from technology → science. Certainly particle physics CANNOT help the materials science of magnets; the latter is essential to the former. Second is the point that a new material, often discovered serendipitously, leads to new science. The extent to which this is true is illustrated by the case of new superconducting materials to BCS and other theories of superconductivity. The latter certainly did not, give an iota of guidance on finding new materials. Yet the discovery by amateur chemistry of 1:2:3 oxide superconductors will provide activity and employment for hundreds of theorists in physics worldwide. Exactly analogous examples may be found in magnetic or ferroelectric materials. New materials certainly are the fountainhead for new materials science.

In the advancement of technology, the story is the same. The new material—teflon, polyethylene, the magnetic garnets, new zeolites—all lead rather directly to new technologies. The feedback loop going towards products requires, in addition, the major components of capital, labor,

entrepreneurship, etc. Any contributions from the science often comes later as an add-on in the second generation of products new zeolites, magnetic bubbles, etc. Thus materials science often helps in the fine-tuning and optimization. But the discovery of the new material is the pivotal point. Had zeolite A not been discovered by Breck et al. (5) an entire industry of catalysts and separation may not exist.

Why then has materials synthesis been so neglected, especially in the U.S.? My analysis of this issue illustrates the necessity for understanding the human dimensions of scientific research. I attempt in this paper to interweave the science with the human and societal dimension. By omitting it I believe we give a false picture of how science really progresses. My studies of why scientists pursue particular topics show the following factors to be most significant in decreasing order of importance. Fashion (based on stories in the popular press), availability of money, local access to particular specialized equipment, the more specialized or exotic, the more powerful the influence. Other factors such as novelty of idea, significance to science, etc., have a very small impact. Few scientists today have even thought about their research in those terms. Thus, in the post WWII U.S., it was the agile and active physics community returning from the Manhattan project that saw the opportunity and took over the field of materials research. They brought with them the incredibly naive and totally spurious notion that basic science (the more the better) "leads automatically to technology and thence to prosperity." [This is a quote from G. A. Keyworth (6), President Reagan's science adviser for seven years]. This notion was built on similar simplistic, later to be proved totally erroneous (7), aphorisms such as "The A-bomb led to the defeat of Japan." And the greatest swindle of all, since Jacob outwitted Esau, that "The bomb was a triumph of science," and not of the incredible power of organized American technology.

Based on these erroneous precepts U.S. national science policy went off on a totally erroneous track as traced by Shapley and Roy in their book (8). Following the ruling paradigm of the day that the more "basic" the science the better, materials science was, in the fifties and sixties, equated to metal physics and solid state physics of idealized alkali halides and similar substances. By the fortunate coincidence of the discovery of transistor action in a new material—highly purified germanium—an ideal marriage of opportunity and availability appeared in the semiconductor world and appeared to support the value of such science. Ge, then Si, in the simple diamond structure, became available in extraordinarily pure and perfect form—thanks to a triumph of materials synthesis. And this opened up the enormous opportunity for the fantastic new science of semiconductors, and the new technologies underlying modern electronics.

In the meantime, in academia and the research-supporting agencies, synthesis of new materials, whether in metallic alloys, ceramics, or polymers was relegated to second class, or worse, status. Theory and phenomena ruled the day. In industry the situation was very different. All corporations remained very active in materials synthesis and processing: Bell Laboratories in Ge, Si, garnets, etc.; GE in new alloys; Lucalox, polymers; Corning in glass-ceramics, photoceram, etc.; 3M in sol-gel fibers

and grains; Philips in ferrites, and so on. At Penn State, the Materials Research Laboratory was the lone exception among major universities with "Materials Preparation" (as the keystone of our clearly articulated research strategy). This put us closer to the kind of materials research regarded as most significant by industry. Hence it was no accident that the Laboratory has had for decades the highest percentage of support from industry among such U.S. laboratories. And for the thirty-year life of the Laboratory and a dozen years before it was formed, we have had at Penn State a major continuing research effort—with several striking successes—in materials synthesis. This long and broad track record was all focussed in the area of ceramic materials. And it is to an examination of the details of what we can learn from these results that we now turn.

DIFFERENT MODELS FOR DOING MATERIALS (SYNTHESIS) RESEARCH

In a lecture such as this I believe it is not productive merely to review the literature on synthesis, or to catalogue our own studies, but to conduct a meta-analysis of the latter to extract insights on the thought processes involved. Our goal here is not to invent new epistemologies, or come up with new theories of innovation or creativity. Rather it is to try to examine clearly the empirical data on 45 years of research on synthesis and see if one can find underneath some common patterns among the successful cases.

We start by making distinctions within the very fuzzy term "science" as it is used in our culture. At least the following three categories of science, S^1 , S^2 and S^3 , can be identified and defined below:

S^1 = Serendipitous discovery (careful observation by highly trained observer).

S^2 = Science for society (purposive, long-term basic science).

S^3 = Science for self and the institution of science.

Next, we turn to determining the relationship of these kinds of science to the motivation or context for the synthesis research. Here also we define three categories, of which the first two are well known:

S.P.: Science Push. This is the concept that the pursuit of knowledge in itself leads to (useful) discoveries.

M.P.: Market Pull. The concept that a need—either in a company or in society—in the "marketplace" for improving a product or finding a better one leads to the advancement. S^2 science based on such market pulls would tend to be narrow in scope and short term. Much new product development research in industry, today, would fit into this category.

T.T.: Technology Traction. This is my own term describing the linking of the new research to a societal need or private market *through* a specific application or technology. Such a "traction" from existing or new devices, hardware, etc., provides a feedback mechanism to the S^2 science from the real application. All such research also

utilizes all relevant "science on the shelf" which will have accumulated partly from S^3 science. It also maintains the S^2 focus for the longer-term science, and hence can, in turn, be sustained for longer periods because it is linked to an existing or definitely needed technology. Much of the *longer-term* research in industry, connected to, or directly relatable to a technology, fits into this category. And it is precisely *only* this T.T.- S^2 research within industry that is by far the most cost-effective and productive component of "research" or science. It was this fraction of the total research spectrum which led to the enormous U.S. technological prowess up through the seventies. It is not fully realized that it is Japan's clear-sighted focus on this T-T- S^2 research which has brought Japanese industry into a commanding position in so many technologies. Unfortunately during the fifties and sixties much of American industry taking its miscue from U.S. academia, conflated its S^2 and its S^3 research. This muddle continues into the present. In the late eighties it became clear that S^3 research supported by industry was simply not justifiable. Regrettably, however, not only S^3 but much T.T.- S^2 research has now been eliminated in U.S. industry demonstration of the urgency for clarifying our terminology, and properly classifying particular research. Figure 6 is a schematic representation of the T.T. process. In many ways it is the realization of the U.S. Defense Department's "basic" or "6.1" research. The imminent downsizing of all industrial research, will be followed, in my estimation, by appropriate similar reduction in S^3 academic research. But this will affect all T-T- S^2 research also unless we start making the distinctions very clearly now.

It is clear that these classifications are hardly sharp and watertight, but they are no less essential for that.

EMPIRICAL ANALYSIS OF LOCAL MATERIALS SYNTHESIS RESEARCH USING THESE CATEGORIES

In earlier papers (1,2), I have alluded to the fact that the basic sciences necessary for a scientific approach to materials synthesis of inorganic nonmetallics are phase equilibria and crystal chemistry. In this respect the U.S. is at a substantial disadvantage compared to the U.K., Europe, the former U.S.S.R., India, etc., since these topics are ignored in chemistry and physics departments and in many materials departments.

This section of this paper is an attempt to analyze the processes by which successful materials synthesis research has actually been conducted in this Laboratory. It analyzes retrospectively using the lens of the categories defined above what actually happened in ten areas where significant

innovation in materials synthesis or processes actually took place. Table 1 gives an overview of the ten subject areas we deal with.

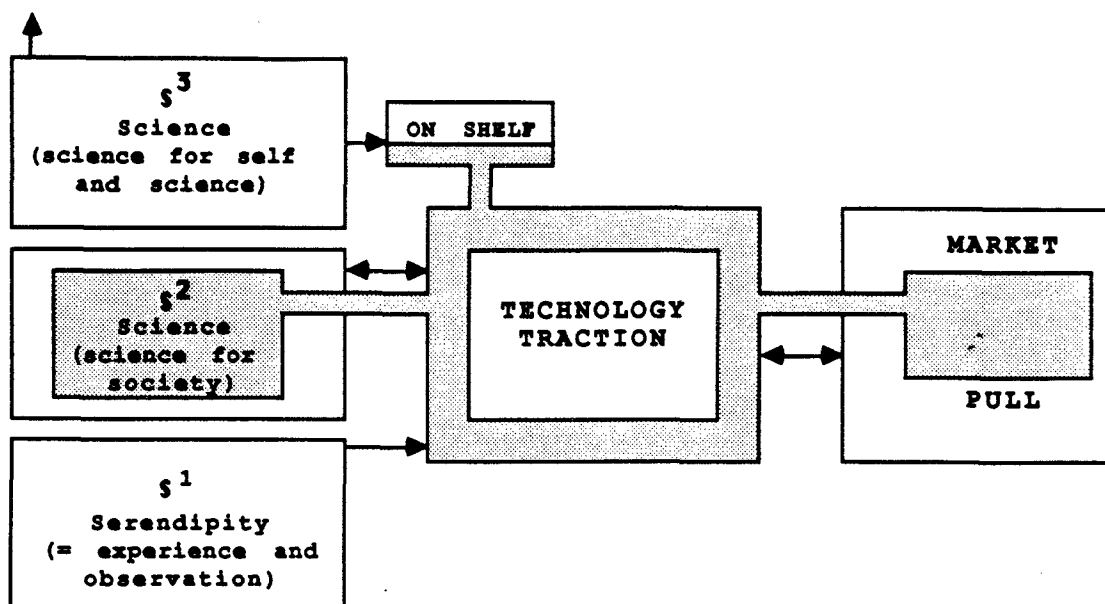


Figure 6. Technology traction model of materials science. In many ways this represents the ideal of what is attempted in the U.S. defense departments 6.1 and 6.2 research.

1a. Hydrothermal Processing; 1b. Sol-Gel Process

These two processing innovations are dealt with together because in fact the basic advances and initial "reduction to practice" were completed in one year (July 1948-June 1949). Together they form a rather clear example of "S.P.," a science-push innovation.

In 1948, hydrothermal techniques had been known for a couple decades as a means of making hydrous phases. The principal "instrument" was the Morey bomb limited to about 400°-450°C and about 1 kbar H₂O pressure. The idea of using water pressure to catalyze anhydrous reactions per se or the hydration of anhydrous phases in the system Al₂O₃-SiO₂-H₂O called for new equipment which could reach higher temperatures. The design of the "test-tube bomb" and multiplexing of several of them with one pressure source created almost a perfect example of the kind of "instrument" to which de Solla Price attributes much of scientific advance. Based on this "instrument," Penn State became the world HQ for systematic hydrothermal synthesis and phase equilibria work for 2-3 decades. It is remarkable to note that this design of the hydrothermal "instrument" has not changed for forty years and the January 26, 1992 issue of *Chemical & Engineering News* carries on its back cover, a full-page

Table 1. Retrospective analysis of "context" of Roy's ceramic research, 1948-1991.

RESEARCH AREA	MOTIVATION	STATUS
• Hydrothermal processes	S.P. To accelerate reactions among oxides at low temperatures	Widely adopted worldwide immediately
• Sol-gel process	To make <i>homogeneous</i> ceramics for all lab research	On the shelf (O.S.) for 15-20 years
• Glass Ceramics		
(a) phase diagram for $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$	S.P. Basic studies in area <i>known</i>	Utilized by Corning
(b) metastable immiscibility	T.T. To <i>be useful</i> in industry	Picked up very slowly
• New zero expansion ceramics	T.T. Clear technology-market pull. Based on major science base.	Applications being explored on wide front after 5-year incubation.
• New methods for fine powders		
(a) EDS	S.P. Improve options for lab powders	O.S. 10 years
(b) RESA		Unpredictable
• Clay mineral synthesis stability.	S.P. Systematic basic work. Known to be useful to oil industry	Used immediately. Fed into industry.
• Zeolite synthesis	T.T.	
• BaO-TiO ₂ phase diagram	T.T. Value of basic science to tech. was clear	Universally utilized rapidly.
• Perovskite $\times 1$ chemistry		
• High pressure materials synthesis/stability (anvils)	S.P. Opportunity push (based on instrument) helped by diamond tech. pull.	No application for any results from hugh worldwide effort.
• Design and synthesis of crystalline radioactive waste Ditto hazardous wastes.	M.P. Apply basic science to obvious societal need T.T.	Strong worldwide impact via regulatory agencies.
• Theory and practice of glass formation in oxides	S.P. Originally basic science of above	Enters general broad stream of activity.
• Thin films. Si, Ge; diamonds	T.T. Pure tech traction	Enormous impact on industry
• Concept of SSG-derived nanocomposites	T.T. New broad concept in our area of expertise	Very rapid entry into science and technology

advertisement for these vessels, still sold by a local firm, with the exact design we optimized within a year or two of its original development.

The **sol-gel process** was also born out of the community's needs in experimental work in oxide systems at low temperatures. The goal was simple and global: To make atomically homogeneous ceramic powders of essentially *any* composition. Without such intimate mixing, in the system being studied ($\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$), reaction rates were essentially zero. Necessity was the mother of invention.

It was clear that mixing via a *solution* step was the only way in which such atomic scale mixing could be achieved. This was already in use for precipitating or pyrolyzing to obtain powders, but gelling ions mixed in solution was the difficult step. To achieve this, I originally used organic precursors for the first time to mix in SiO_2 , Al_2O_3 , TiO_2 , etc. Later inorganic sols with 20-100 nm particles proved to be equally efficacious. The conceptual advance was the use of a gel step instead of a glass step (then in common use in high temperature silicate equilibria studies, but limited to glass-forming compositions). Here again although it was S.P. research, there was a distinct generic experimental "need" which was being addressed at the same time. This makes a kind of connection to a T.T. type research. What is truly remarkable about the sol-gel process is, first, how completely successful it was. Within a decade our Laboratory files held vials of **several thousand** compositions in dozens of simple and complex oxide systems made by several different investigators and described in dozens of papers. Secondly, it was remarkable how long it took for the sol-gel method to be picked up by the ceramics community—nearly 15 years in industry and 25 years in academia. This, in spite of the fact that the large number of papers had been published by the Penn State groups and the world-wide geoscience community.

2. Glass-Ceramics: This is an Excellent Combination of S.P. and T.T.

My connection to glass ceramic research came about entirely serendipitously because my Ph.D. thesis was the detailed phase diagram for the system $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$, including the spodumene-eucryptite join. Simultaneously with this study my colleague, F. A. Hummel, discovered the extraordinary low and negative thermal expansion of the eucryptite and spodumene phases. Stookey at Corning after his doubly serendipitous discovery of the glass ceramic process, of course, utilized Hummel and Roy's work in making the first commercial glass-ceramics, Corningware.

Thus our S.P. contribution was prior to Corning's discovery of the process, but our further contributions were strongly pulled by the T.T. process since many other corporations such as Pfaudler and PPG turned to us for collaboration in their glass-ceramic research. Their goals were met in a very short time. Our subsequent contribution to **understanding the glass-ceramic process** came from our phase equilibria studies on titano-silicate systems. Thus in pure S.P. research, DeVries, Roy and Osborn (8) first totally revised the phase diagram of the system $\text{TiO}_2\text{-SiO}_2$ from supposedly having zero liquid

immiscibility, to nearly 80% immiscibility. And their work on the CaO-TiO₂-SiO₂ (9) system outlined large areas of stable liquid-liquid immiscibility, bordered by large regions where enamel-like glasses formed. This led me to the key paper (10) on the role of metastable liquid immiscibility as the correct nucleation step (correcting Stookey's original and sometimes still reported, assignment of the nucleation step to "rutile" formation). The two highly relevant phase diagrams are shown in Figure 7. One of the issues in contemporary synthesis research is the general weakening in the materials community of the ability to interpret especially more complex phase diagrams and the absence of classical crystal chemical knowledge.

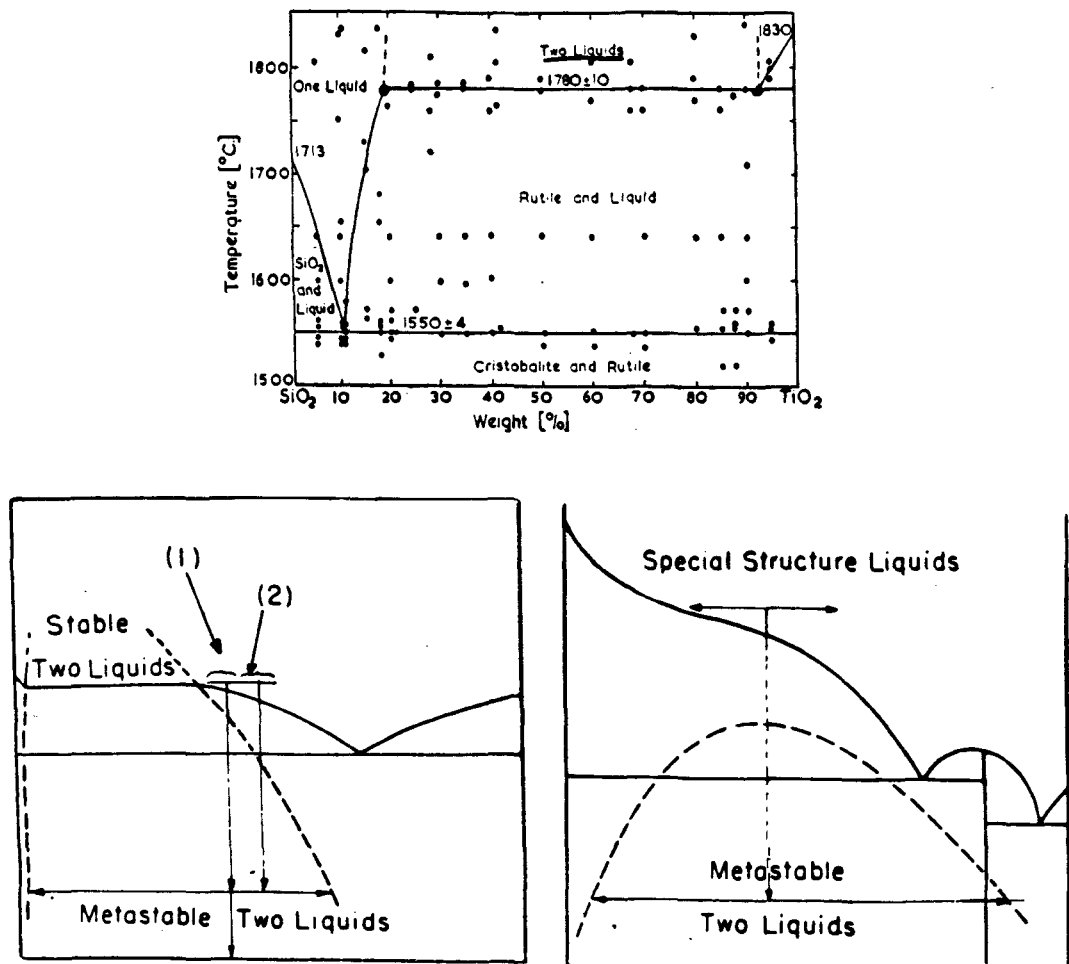


Figure 7. The role of liquid-immiscibility in TiO₂-rich silicate melts was hinted at from the phase diagram for the system TiO₂-SiO₂ (and CaO-TiO₂-SiO₂ not shown) and *metastable* mixing of two liquids explicitly identified as the nucleation step in such glass ceramics.

3. Zero-Expansion Ceramics: A Model T.T. Success in Synthesis

This is one of the clearest examples of a technology traction development. Because of our involvement with the initial discovery of the major zero expansion materials of commerce the lithium aluminosilicates (LAS, see above), the Air Force Office of Scientific Research approached us to try to develop a new material with thermal expansions even closer to zero at -100°C for space structures. Here was a clear market pull, well-established technologies existed that could use such materials and while much new data on new materials had been accumulated in the 40 years since the LAS discovery, no other crystal structure had even begun to compete. Our approach proceeded sequentially:

1. Modifying, compositionally, a known near-zero α material: cordierite. By using sol-gel processing we were able to introduce more Ge than hitherto achieved and obtained some very acceptable low α phases (see Ref. 11).
2. "Theory" was totally useless in helping locate an inherently anomalous structure. By serendipitous observation, using our own empirical guidelines (structures articulating strongly $4+$ and $5+$ valent cations), bonded polyhedra around large "holes") we discovered the low- α properties of a very well known structural family, the NZP ($\text{NaZr}_2\text{P}_3\text{O}_{12}$) or CTP ($\text{Ca}_{0.5}\text{Ti}_2\text{P}_3\text{O}_{12}$) family (Refs. 12-14). We were able to show that a dozen different compositions completely bracketed the low+ and low- α range, with extensive solid solution allowing every value in between (Figure 8).

THERMAL EXPANSION OF [NZP]-FAMILY

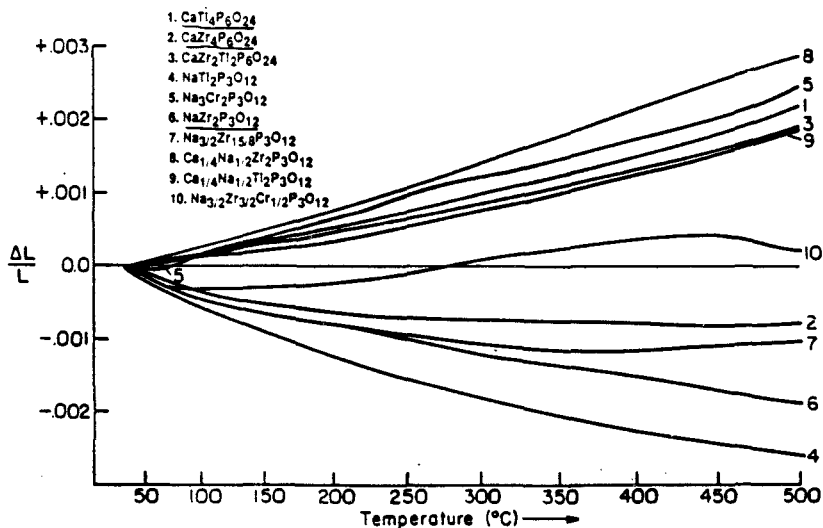


Figure 8.

Success with this objective led the AFOSR to set another: eliminate the anisotropy of α if possible. There appeared to be no rational process to eliminate the anisotropy of α in the hexagonal phase, since it is by averaging a negative α in "a" or "c" direction with a positive α in the "c" or "a" direction, that we get zero. But another serendipitous observation (that in $\text{Sr}_{0.5}\text{Zr}_2\text{P}_3\text{O}_{12}$ the "a" and "c" axes were reversed) led us to the "zero"- α , "zero"-anisotropy $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ family which also turned out to have melting points above 1700°C (14).

3. The third objective given to us of making a ferrimagnetic NZP phase to absorb radar signals (market pull) appeared like a reasonable challenge due to the fact that most 3d and 4f ions can be accommodated in the structure. Yet, in spite of very extensive experimental substitution, this approach did NOT work. We were unable to synthesize any ferrimagnetic NZP phase. Instead, we had to design a microcomposite of two thermodynamically compatible (determined experimentally) phases, one with a negative α ($\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$) and a ferrimagnet (YIG) with a positive α .

The NZP family of controllable low expansion ceramics is an outstanding example of systematic T.T. materials synthesis. There are obvious technological opportunities for such materials but the actual penetration into established markets will be decided by many other factors outside science. This example is almost a textbook case of T.T. practice at its best—which is, of course, NOT universally successful. It demonstrates the value of having access to an "on-the-shelf" science base—in our very long experience in the field. And it demonstrates that "theory" is not of much help in designing new materials. And finally, it proves the value of serendipity based on careful observation by experienced observers who can recognize anomalies and pick up hints in not directly related literature.

4. Processes for Making Fine Powders (S.P.)

In the early fifties in parallel with the sol-gel processes we had also experimented (15) with spray pyrolysis of the mixed solutions. By a decade later Ruthner (16) had exploited the same process and made it into a successful commercial process for making ferrite and alumina powders. We showed that the EDS or DMS (decomposition of mixed solutions) process had both general and special applications in powder preparation in the laboratory also (17). However, in spite of the enormous interest in ceramic powders, few really new methods have appeared in decades. The laser pyrolysis approach had proved to be very limited in the range of ceramic powders which can be made and very costly. This "need" in science and technology provided the very diffuse pull for our work. The concept of the "reactive electrode submerged arc" (RESA) (modified after the classical work of Faraday on

making gold sols) works by striking an arc under water, solutions, organic liquids, silicones, etc. The apparatus is shown in Figure 9.

The RESA process has proved to be quite general (18) for making pure submicron powders of oxides, carbides, nitrides, and very recently (unpublished) of new crystalline carbons related to Buckyballs. It represents a successful science push development, not yet linked to a technology, but has obvious potential for special application. And a recent development, the so-called "combustion synthesis" developed in India, appears to be another really novel process (19) for making fine powders.

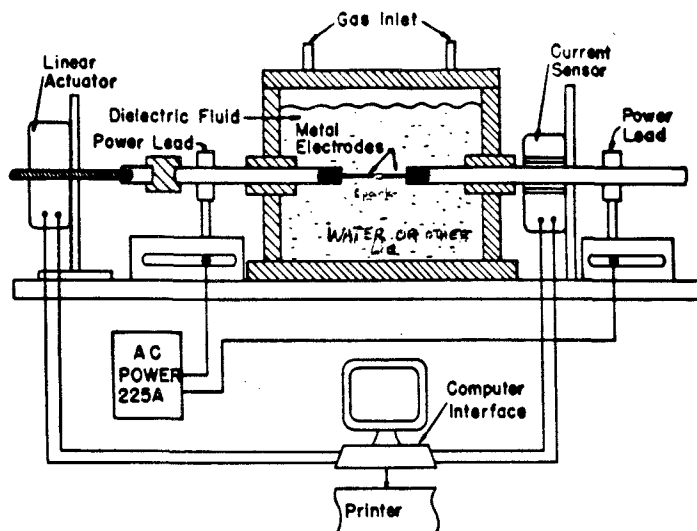


Figure 9.

In all such S.P. advances that we have made to date an important common characteristic is the **discontinuous break** with the past. S.P. advances in synthesis or processing occur **far from mainstream activity** and therefore are very likely to be missed and ignored for years. This again argues the case for scouring the literature on the **periphery** of one's interest to pick up hints or related advances which may have been already demonstrated in other connections.

5. Clay and Zeolite Synthesis (S.P. + T.T.)

We have noted that the first application of the hydrothermal instrumentation was to the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ for the catalysis of subsolidus equilibria among anhydrous phases, and studies of the synthesis (and stability) of the hydrated clay minerals (kaolinite and pyrophyllite) in the system. With that beginning, we launched a ten-year emphasis on the synthesis and stability of all clay

minerals first in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and later with the systematic, step at a time, addition of alkali (K, Na) and alkaline earth (Ca, Mg) oxides as an additional component.

Figure 10 gives but one example of two dozen of the kind of detailed phase equilibrium "maps" (this one for the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$) which we produced, at enormous personnel cost by today's standards, as the permanent template to guide all such synthesis efforts. Alongside this S.P. science, we were able, for the first time, to create entire suites of di-octahedral (Mg) and tri-octahedral (Al) sets in the 7\AA , 10\AA and 14\AA mica and clay mineral families. Both expanding and non-expanding

$\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

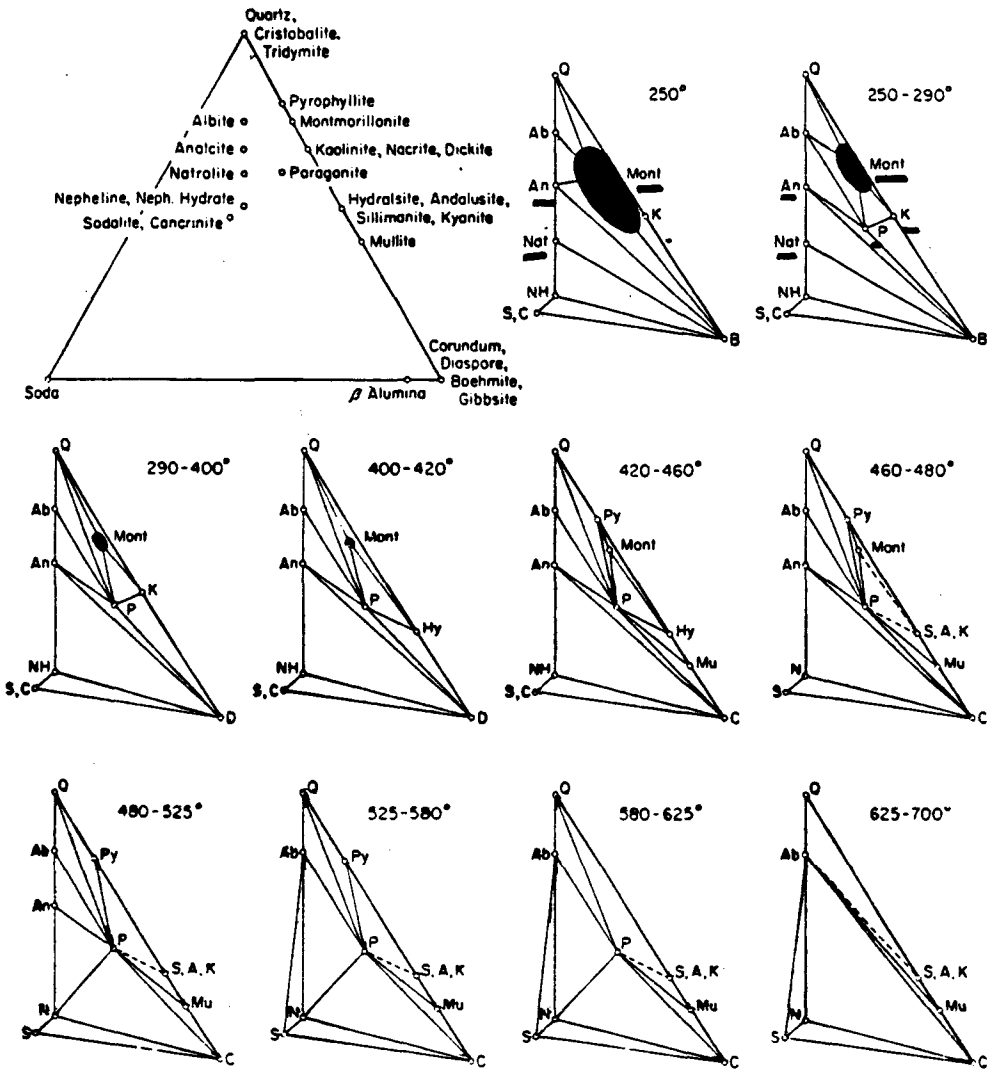


Figure 10.

10Å minerals of completely controlled charge density were synthesized in various systems including exotic ones involving Ni, Ga, Ge, Zn, etc. The demand for this depth of basic work was, of course, due to a T.T. linkage to the petroleum industry's interest in clay minerals both as stratigraphic markers and as drilling muds.

Even in the mid-fifties we were able to even control the morphology of micron size powders from high aspect ratio fibers, to equant hexagonal flakes [see Roy and Roy (20)] by compositional manipulation (i.e., Al^{IV} and Al^{VI} substitution for Mg^{VI} and Si^{IV}).

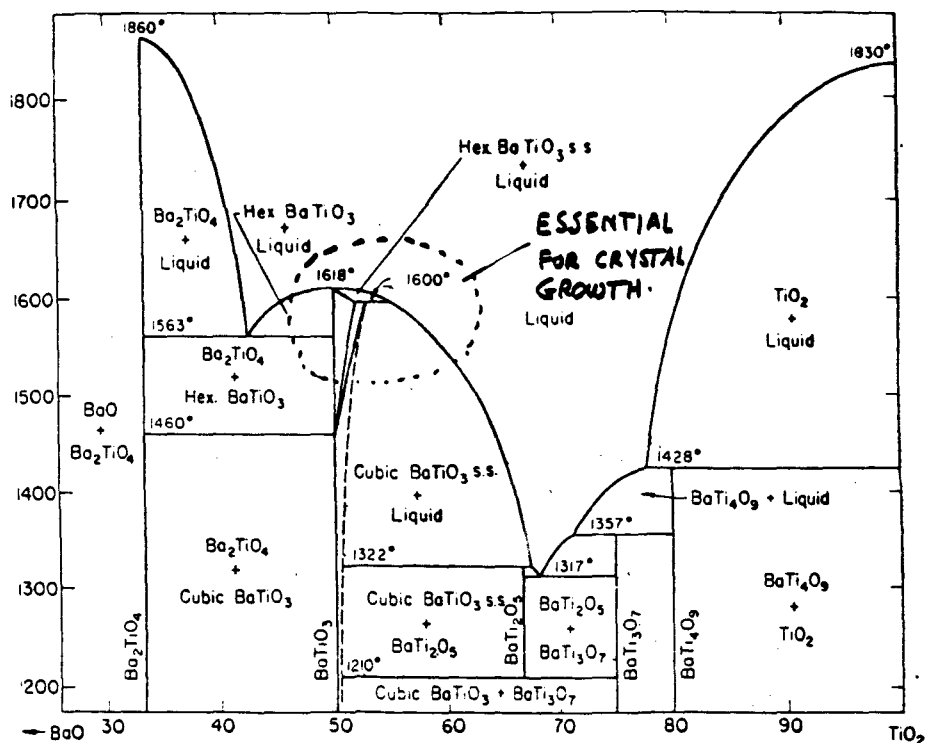
Following the *systematic* clay syntheses, we pursued the same strategy on the *known* major zeolite families. Systematic detailed studies of the synthesis and stability of the phillipsite, analcite and mordenite-wairakite families were carried out in the hydrothermal regime. Even after the Union Carbide discovery of zeolites A and X, due to the highly proprietary nature of the work, in spite of our obvious expertise, we were not invited by industry to be involved in the race to create new zeolites, i.e., there was an insufficient T.T. element to channel our synthesis capabilities into possibly fruitful directions. Our zeolite syntheses therefore "stayed on the shelf."

6. Perovskite Electroceramics (T.T. and S.P.)

This area constitutes a first-rate example of using all our knowledge base to put materials synthesis of an important new family of materials on an intellectually sound basis. The U.S. Army Electronics Command recognized the need (a) to grow single crystals of BaTiO₃ and (b) to look for similar phases which might be even more useful. In the early fifties there was enormous research activity in applications of such phases to capacitors and the technology traction feedback loops were active and *rapid*.

For task (a) it was realized that a reliable phase diagram was essential. Figure 11 shows the phase diagram for the system BaO-TiO₂ which were determined by us, the first such detailed high temperature equilibrium diagram of a titanate system with any degree of reliability. And it was on the basis of this diagram that Linz et al. at MIT were then able to grow the first reproducible large single crystals of BaTiO₃. Here was S.P.-T.T. coupling across institutions.

For task (b), we worked in the V. M. Goldschmidt tradition of empirically determining the structures of a large number of rationally engineered (with respect to composition) candidate phases. From the structural data we were able to provide structure field maps for future materials synthesizers in search of a particular phase. See the book by Muller and Roy (21) for a compilation of such SFM for all ternary ceramic structures. Our crystal chemical study on the perovskite structure (22), for example, besides lists of very much-used substitutions, shows the first of the phases Ba₃NiTa₂O₉ prototypical of the PMN (Pb₃MgNb₂O₅) or relaxor ferroelectric materials, which have now become possible successors of BaTiO₃ in certain applications.

Figure 11. BaO, TiO₂.

7. High Pressure Materials Synthesis: Pure S.P. Syntheses with no Spin-off

Although in the mid-1950's we were the leading laboratory in the hydrothermal high pressure regime (up to a maximum of say 10 kbars) we had failed to synthesize any of the high pressure minerals (kyanite, jadeite, pyrope, and of course diamond) mineralogists had set their sights on. With the work of Coes at Norton and Hall at GE, two new kinds of apparatus—the piston-cylinder and belt—were developed which enabled one to reach the P-T regime for synthesis of all minerals occurring on the surface of the earth. Again, the "instrument" played the key role.

Yet these apparatuses were extremely expensive and time-consuming to operate. Hence we chose to develop instead Bridgman's simple and compound anvils as a simple "instrument" for use in materials *synthesis*, at very high pressures (~200kbars) and modest (~500°C) temperatures. Our

opposed-anvil apparatus proved to be a very effective and reliable tool in materials synthesis [see Dache and Roy (23-25)] and also became widely used. Indeed later on the utilization of single crystal diamond as the anvils by van Valkenburg at the National Bureau of Standards led eventually to the work of Mao and Bell at the Geophysical Laboratory in reaching megabar pressures at $\approx 2000^\circ\text{C}$ temperatures to study in-situ transformations especially those related to the interior of the earth. The diamond anvils have not produced many new quenchable phases.

Our opposed-anvil apparatus allowed us to synthesize—by 1970—more new high pressure materials (which could be retained at ambient conditions) than all other laboratories combined. On the other hand, our own crystal chemical studies on the effects of pressure showed that there was no scientific reason why high pressure would lead us to new structures with extraordinary properties. The logic of each of our structure field maps showed that whatever structures could only be achieved with pressure at a **certain composition**, could be often created at 1 atm pressure merely by changing the composition. Hence nothing especially interesting should be expected among high pressure phases with the single exception of diamond which is the unique extremum in composition in the middle and top of the periodic table.

In the event, we were proved correct. No product of any value, no technology, has emerged from the extensive worldwide high pressure program. This was quintessential S.P. materials research which led only to “science on the shelf”; in geophysics the results proved to be very stimulating of new hypotheses about the mantle.

8. Materials for Radioactive Waste Immobilization; Excellent Example of M.P. (T.T.)

This area is an extraordinarily apt example to illustrate the relationship between society's needs, and universally expressed desires from the world of science and technology, and how the U.S. system of R/D actually responds.

Reading in the general press about the enormous public anxiety about nuclear waste and the national plans for the solidification of radioactive waste, it became clear to us before 1970 that modern ceramic materials research could be brought to bear on the problem. To our astonishment, in spite of the enormous public and vocal “market pull” in this very visible area, quite literally zero research was being done on examining alternative solids in which to contain the radionuclides. The design scenario in 1976 (more or less tacitly adopted by all nations worldwide) was to melt the radionuclide mixture into a borosilicate glass, fill the molten glass into steel canisters 3m \times 1m diameter, and dispose of these in selected rock formations (either salt or shale) with equilibrium centerline temperatures of 500°C (or more).

In a few months of preliminary work we established two key facts:

1. That the projected glasses would totally decompose in times of about 1 week if exposed to any water at the proposed repository temperatures. The one-page paper we published in *Nature*

(26) had probably more *technological* impact than any single equivalent recent scientific paper. It forced every nation to redesign their waste form by diluting the radioactive content. Thus, this multiplied the volume of glass waste 3-4 times, and hence increased the *projected* repository area and cost proportionately by billions of dollars.

2. In the second paper [McCarthy et al. (27)] we proved that an ordinary multiphase crystalline *ceramic* (as in a porcelain or brick) could be made to incorporate all the radionuclides of reprocessing waste.

Only after this S.P. demonstration on two fronts was the M.P. strong enough to actually start a modest national research program on alternative solidification. Yet, and this is enormously significant, since there was no technology in place, the M.P. could only sustain the program for five years. This shortlived research effort (worldwide) on novel ceramic waste form synthesis produced notable successes including Oak Ridge's Fuetap cement, Penn State's first tailored ceramics and Australia's synroc subset of the tailored ceramics. (See Table 2 for details.) While it lasted, excellent science started to provide the kind of data the technical community and the public wanted, the scientific data on synthesis stability and leachability and the related data needed to make a judgment on quality of product and costs with these alternative forms [Roy (28,29)]. But the Reagan Administration decided—since alternatives would take time to study—to proceed with the most advanced-in-engineering form—borosilicate glass—in order to “complete the job” on a totally unrealistic time schedule. A decade later, in an area where the total costs will run into the hundreds of billions of dollars, no glass technology exists, no alternative waste forms are being studied nor waste form options for commercial waste. And we are no closer to acceptance of *any* solution and this materials component of the research is not yet done. So much for the efficacy of M.P. in the absence of T.T. in sustaining synthesis research.

9. Ceramic Thin Films From Glass Formation to Diamond Films (S.P. to T.T.)

When we started our research on thin-films in the 1960's probably few ceramic thin films existed in technology; the science was non-existent. Sol-gel derived noncrystalline films were starting to appear as coatings on windows, and MgF_2 coated lenses were being modified by other oxide optical coatings on glass.

Our interest in the thin film form of ceramics derived from the vapor, was that it would offer a new way to create noncrystalline phases from compositions which could not normally be so rendered. By (splating and) sputtering we were in fact able to create a wide range of such new glassy materials. But then the interest shifted to being able to prepare unique thin film glassy or crystalline ceramics (including Si, Ge, CdS, etc.) by utilizing RF sputtering onto virtually any substrate. This gave us the ability to create very interesting new materials such as hyperdense noncrystalline Ge (30-32) which could be crystallized “explosively” at room temperature by a mechanical or thermal trigger pulse. It also started the work to determine the processing conditions to yield thin film crystalline perovskites

Table 2. Ceramic radionuclide containment.

Structure Type	Illustrative Compositions	Possible Radionuclides and other f.p. incorporated		
		Total	Major	Minor
A. "Insoluble" Mineral-Modelled Phases				
[Monazite]	(Ln,Al ³⁺)PO ₄ An ⁴⁺ SiO ₄ (Ca _{0.5} An _{0.5})PO ₄	Ln,An		
[Perovskite]	(Sr,Ba)(Ti,Zr)O ₃	Sr	Ru,Tc ⁴⁺	Ti,Cs,An,Ln
[Pollucite]	Cs,AlSi ₂₀ 6	Cs		
[Spinel]	(Ni,Fe)(Al,Fe) ₂ O ₄		Tc ⁴⁺	Ru
[Apatite]	(Ca,Sr) ₅ (PO ₄) ₃	Sr		Ru
[Scheelite]	(Sr,Ba)MoO ₄	Sr	Tc ⁶⁺	Ln,An,Ru,Te
[Feldspar]	SrAl ₂ Si ₂ O ₈	Sr		
[Fluorite]	(An,Ln,Zr)O _{2+x}	Ln,An		Sr
[Zirconolite*] (ordered fluorite)	CaZrTi ₂ O ₇	Sr	Ru	
[Rutile]	RuO ₂	Ru,Te		
[Fcc Metal]	Pd			Pd
[Hollandite*]	BaAl ₂ Ti ₆ O ₁₆		Cs	
[Nepheline]	NaAlSiO ₄			Cs(?)
[Barium-aluminate* iron titanate]	Ba(AlFe) ₂ Fe ₈ Ti ₁₃ O ₃₈		Cs	
[Magnetoplumbite*]	BaFe ₁₂ O ₁₉	Sr	Cs	
B. Tailored Ceramic Assemblages to Accommodate PW-4b Waste Ions				
High concentration of fission products	(i) + scheelite + fluorite + pollucite + apatite + corundum			
	(ii) + scheelite + fluorite + pollucite + zircononia + monazite + corundum			
	(iii) perovskite + fluorite + pollucite + monazite + spinel			
Low Concentration of fission products	Zirconolite + perovskite + hollandite			

(33)—especially high K materials such as BaTiO₃. Sputtering also provided an easy route to synthesize a whole range of crystalline or noncrystalline solutions of ceramics in one run simply by using two targets or mixed targets (32).

When the synthesis of BaBiPb oxide superconducting perovskite was announced by Sleight et al., we began the first systematic study to attempt to raise the T_c by crystalline substitution. The sputtering process for producing the first crystalline ceramic superconductors was described by Gilbert, Messier and Roy (33) nearly ten years before Geballe et al. (34) reported on similar sputtered films of the 1:2:3 composition perovskite.

Up to this point our substantial thin film effort had been driven mainly by S.P. Some T.T. work had been incorporated in attempts to apply these techniques to electrochromic films of WO_3 . But it was in 1985 that a radical transformation occurred when I personally encountered the successful CVD diamond film work at NIRIM in Tsukuba, Japan, and at the Institute for Physical Chemistry in Moscow. After convincing skeptical agencies, and supported by the Office of Naval Research in a T.T. model, we drove the system into a major effort of understanding the process of making CVD diamond thin films (35,36) and transferring our knowledge about them effectively. Our diamond film synthesis effort has been **comprehensive**, to be able to compare all the methods for diamond film synthesis; and **evaluative**, not advocating one or other method or explanation or theory. This stance has allowed us to observe how slowly indeed real progress is made in materials synthesis. Today after hundreds of person years of research, the original Derjaguin and Fedoseev discovery (theory) of using atomic H to dissolve graphite and retain diamond (37) lies at the heart of every process in use (see Review 35). The original Japanese utilization of microwave plasma (and hot filaments) still is the standard method (38). The most novel addition has been Hirose's (39) utilization of the oxy-acetylene torch. The extensive theoretical and modelling research—as in all cases of materials synthesis—has proven to be so far without any redeeming social or scientific value. Research managers must face the empirical reality that here, as in 1:2:3 superconductors, in ferroelectrics, in new magnets: **theory and models have provided zero guidance to any synthesizer.**

Our local research contributions so far include the creation by Badzian et al. of rather perfect homoepitaxial diamond films which, when diamond was featured as the first "Molecular of the Year" in 1991 graced the cover of *Science*, and also some of the first diamond electronic devices (40) based on such films.

10. Nanocomposites and Their Formation Via the SSG Route (S.P. + T.T.)

In a series of presentations in 1983 and 1984 I presented (41) an approach to the synthesis of an entirely new *class* of materials which I termed **nanocomposites**. My argument ran as follows. All traditional materials synthesis and processing techniques—sintering, melting, etc., must allow enough kT energy to equilibrate the total composition involved on at least the scale of micrometers or tens of micrometers.

In other words, in known multicomponent-single phase and multiphasic materials (except certain alloys with post formation heat treatment) the size of the phases are at least on that scale. On these scales the two phases do not interact with each other with respect to chemical, structural, and most electrical, optical and magnetic properties. Bulk properties are averages or additions. If we could reduce the scale of mixing—I argued—to the nanometer dimension, we would be able to create a **hybridization** of properties of two phases. Moreover, if one could use low temperature processes to synthesize such "nanocomposites," radically different phases, very far from equilibrium with one

another could be mixed with one another. This change of direction for SSG research has been described in context in a review (42). At approximately the same time E. Gleiter at Saarbrucken was reporting his own work on the very interesting advantages of simply reducing the size of particles of a single phase to nanometer dimensions (43).

Our earliest attempts to create such nanocomposites were to use two target sputtering, to combine Al_2O_3 with Au, or platinum with teflon or polyimids. These gave rise to interesting combinations of 1-2 nm size metal particles, some with 5-fold symmetry (44) in an insulator matrix. The process, however, was tedious and the only form which the materials appeared in was as thin films.

It was then in 1983 that I re-entered the world of solution-sol-gel research which worldwide was now addressing universally the goal I had set for myself in 1948, viz: to make **maximally homogeneous** ceramics. My new goal was to create **maximally heterogeneous** ceramics (i.e. with the maximum interface area of two or more phases) by the SSG route (see Ref. 42). In the next several years, making *nanocomposites* became a major research area in our laboratories (45-47). Our Japanese colleagues held the first international conference on the topic in 1989 (48) where very interesting new composites, created and studied, were reported on. Our original efforts and these results signal that nanocomposites may well have as substantial an impact on the field of ceramics as did the original sol-gel work.

Our own research in SSG-derived nanocomposites has demonstrated that—by the simple universally accessible expedient of mixing two sols—one can achieve the entire set of processing innovations shown in Table 3. Two interacting phenomena explain all these chemical-structural effects, the effects of chemical heterogeneity and structural heterogeneity (Table 3).

Table 3. Nanocomposites will certainly offer a family of new materials with improved properties in various applications. Our work has demonstrated such improvements in the chemical/structural area. The work of others has started to provide examples of real improvements in other properties.

What can nanoscale mixing achieve? In different properties?		
Chemical/Structural	<ul style="list-style-type: none"> • Control of phases formed • Lowers reaction and sintering temperatures • Control of microstructure • Control of morphology • Via solid state epitaxy 	Our studies
Mechanical	<ul style="list-style-type: none"> • Five-fold increase in strength as size goes from 100-20 nm • Suprahard (>diamond?) materials 	Work of others
Optical	<ul style="list-style-type: none"> • Ten-fold increase in luminescence 	
Electrical	<ul style="list-style-type: none"> • Change in fundamental conduction 	
Magnetic	<ul style="list-style-type: none"> • New super-, para-, and ferri-magnets 	

1. Compositional Heterogeneity

Such composites may make possible exothermic and rapid reactions of two intimately mixed phases far from equilibrium with each other. For example, one may contrast these classes of mixtures of, say, $\text{Al}_2\text{O}_3 + \text{SiO}_2$ at the mullite composition (or $\text{ZrO}_2 + \text{SiO}_2$ at the zircon composition):

- (a) Mixed 325 mesh powders of Al_2O_3 and amorphous SiO_2 .
- (b) Single homogeneous liquid solution made into an atomic scale homogeneous (one phase) solid (xerogel) solution.
- (c) A composite of 1-10 nm size particles of Al_2O_3 and SiO_2 (diphasic xerogel).

Mixture (a) heated at, say, 1250°C for 1 hr will show no measurable reaction by XRD, and little in TEM except perhaps in the reaction rim around some of the grains. Mixture (b) would show a high percentage of formation of mullite but mixture (c) would show the highest percentage of well-crystallized mullite.

The explanation lies in the fact that the diphasic xerogel has the advantage that the reaction of Al_2O_3 with SiO_2 is auto-catalytic because it is exothermic, due to the $\Delta H_{\text{reaction}}$. In the monophasic gel, the reaction rate is much slower because the only ΔG available to drive is the ΔH of the noncrystalline \rightarrow crystalline transition. Generically compositionally heterogeneous nanocomposites utilize the heat of reaction of the metastable \rightarrow stable assemblages.

2. Structural Heterogeneity

The idea of seeding gels with desirable structural templates goes back to the very first year (1948-49) of the discovery of the SSG process and hydrothermal process (49). We used 10-50 μ size crystalline templates as one phase and noncrystalline xerogels as the other. In these early papers we demonstrated the successful overgrowth on such phases as diaspore, α -spodumene, benitoite, etc., in hydrothermal reactions. Here one could assume the second phase with the "right" crystallography was serving as an epitaxial substrate for material transported via the liquid phase. Thirty years later crystallographically seeded xerogel nanocomposites showed remarkable effects on the kinetics even of solid state reactions completed in minutes or hours.

3. Combined Structural and Compositional Homogeneity

An additional wrinkle in utilizing such composites is to make them tri- or tetraphasic and combine both the compositional and structural inhomogeneities in the composite.

In the last 8 years we have demonstrated the large effects which can be caused on materials synthesis by these simple experiments in many systems: alumina; mullite; zircon; thorite; cordierite. Figure 12 is a schematic summary of the temperatures to achieve equivalent formation of ZrSiO_4 from

various mono-, di- and triphasic xerogels. The advantage is clearly very substantial: lowerings of about 250°-300°C.

Solid-State Epitaxy

Finally, in the early diphasic work we unequivocally established the fact that the efficacy of structural di-phasicity (seeding) was due to crystallographic epitaxy. This was done by using seeds of different structure and demonstrating that only the one with the structure of the product phase was effective. The effects could *not* be associated with just overall heterogeneous nucleates (46,49). However, another approach provided complete proof of the phenomena of solid state epitaxy. In recent papers (50) we have grown very highly aligned crystals of the product phase (TiO₂, SrTiO₃, Al₂O₃, PZT, PMN, etc.) onto large (cm size) single crystal substrates of the same phase. Indeed utilizing the "solid" state epitaxy principle, it has been possible to crystallize *albite* (NaAlSi₃O₈) from a di-phasic gel made from its own glass with crystalline albite seeds. This is possibly one of the most difficult glasses in existence to crystallize (51).

We have also shown that by using the appropriate crystallographic template one can drive the reaction to different products—either metastable or stable assemblages (e.g., ThSiO₄ can be crystallized at 1400°C to either the huttonite or thorite structures. And by controlling the composition one can control the morphology of the final product phase (52).

Crystallization begins in ZrSiO₄ at

		<u>Compositionally</u>	
		Homogeneous	Nanocomposite
<u>Structurally</u>	Homogeneous	1350°C	1175°C
	Nanocomposite	1100°C	1075°C

Figure 12. Efficacy of nanocompositing in starting material in lowering reaction temperatures in various mono- and di-phasic gels. The reaction of crystalline ZrO₂ and SiO₂ would be very small at these temperatures.

Outside our work on chemical structural effects we can see that compositional and structural engineering at the nanolevel is certain to become a routine powerful tool in ceramic processing from the results reported in Ref. 48. No better demonstration can be found than in the dramatic results achieved by Niihara et al. (53) in all the mechanical properties of engine ceramics (Al_2O_3 , SiC, sialon) by the use of nanoscale dispersions of second-hard phases.

NEW MATERIALS SYNTHESIS: FUTURE DIRECTIONS

SOME BLIND ALLEYS: CONTROLLED DESIGN OF NEW MATERIALS

In Figure 4, I summarized the capability we have to create new materials. It is self-evident that in any mature technology, the combination of two or more materials always will do better than one. It is well established for all mechanical applications that composites do vastly better than single phases. The initial success of discrete silicon devices was soon eclipsed by composite structures on a micrometer scale of the chip technology. Optical fibers are all graded composites.

But what is the potential of synthesizing by design a completely new crystal structure, at the unit-cell level with desirable optical, magnetic, superconducting properties? Again, however hard it is for the scientist and the manager to accept, the empirical track record is unassailable. Our capacity is nearly zero. No better example can be found than the worldwide search for new superconductors. After the first public announcement by Zhao (53) of high T_c phases in the system Y_2O_3 -BaO-CuO found by sheer empirical mixing and measuring, it was a matter of one or two person weeks of work in several different laboratories in IBM, AT&T and Bangalore to isolate the $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase. But since then, after some thousands of person years, with full benefit of theory, with no shortage of equipment or money, the world's synthesis communities have found exactly zero really new structures outside the 'perovskite + Cu-O layers' family. The recent serendipitous discovery of superconductivity in Rb_3C_{60} and Cs_3C_{60} Buckyball compounds, confirms the total scientific ignorance in our theory of synthesis of really new phases with desirable properties.

The original serendipitous discovery of the magnetic rare earth garnets in 1954 by Keith and Roy (55) did not equip us or any of the enormous range of extremely competent magnetic materials groups in the world to design or even to find, in 40 years, any comparable 3 sub-lattice structural families with similar ferrimagnetism. The new rare earth iron borides again were a unique and serendipitous discovery with little transferability of knowledge, and again, surprisingly, no follow-on success.

In 1992 we must therefore admit that it is not possible to synthesize any new phases with different crystal structures, with specifically desired properties, based on any theories or models. Even serendipitously discovered new materials provide but little empirical guidance for tinkering with neighboring compositions and obvious substitutions.

BLIND ALLEYS II: BIOMIMETICS; BIOGNOSIS

In the last year or two as the publicity surrounding quasi-crystals and cold fusion subsides, a wave of publicity has been created to suggest that one *might* make useful new materials by *mimicking* nature. The extraordinary gullibility of the present-day scientist community is evidenced in the reception to this idea since it is never presented based on a single, even modest, achievement. Yet, surprisingly no synthesis of any material with any extraordinary or useful property has been reported by all those who advocate the value of this route to new *biomimetic* materials (56). To the best of our knowledge, only one single useful material which can by any stretch of the language be called a biomimetic material, has ever been made. This is the replamine process by E. W. White et al. in this laboratory, who mimicked a South Sea coral in its key external morphology of a 3:3 connected structure. From this they made both biomaterials for dental and bone implants, and exactly mimicked the morphology of the same materials (see Fig. 13) using them as templates for making biological and electroceramic composites (see 57-59).

The implication in the oft-repeated appeals, that Nature, which optimized its materials for low temperatures (<50°C) and aqueous environments, would provide some miraculous templates for mimicking to make materials for airframes, or superconductors, or magnetic or optical materials, smacks, as Professor Jonathan Black of Clemson (60) remarks, of a return to the philosophy of "vitalism." The empirical facts are exactly the reverse. Materials science and technology have

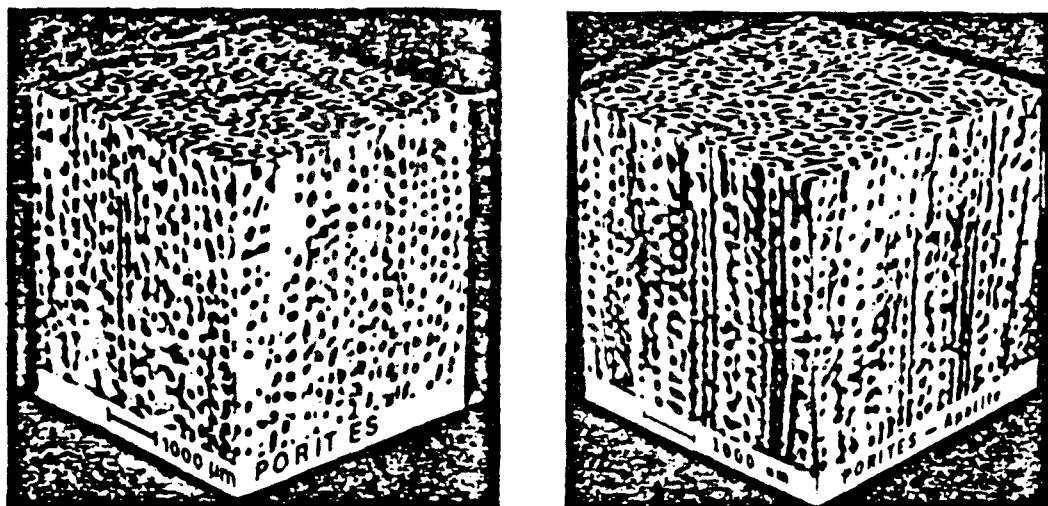


Figure 13. Three-dimensional SEM photograph of original coral (var. Porites) made of CaCO_3 on the left, and the exactly copied biomaterial on the right after transformation under hydrothermal conditions to apatite. This is the only example of a commercialized biomimetic material known.

provided enormous help from non-bio-derived materials for the human biological system: Metal, polymer and ceramic parts for teeth and bones; polymers for skin and other soft tissue, etc., are ubiquitous and unlikely to be displaced to any large extent by bio-derived solids.

This is not to say that the materials designer and synthesizer may not have **much to learn from**—not necessarily to mimic—nature. I have termed this process **biognosis**. Here again one must note that the extraordinarily detailed studies by the three or four British schools, of Vincent, Currey, Mann, Birchall, etc., which have *described* biological hard tissue in great detail over the last 10-20 years have as yet to synthesize their first novel material based on such learning. If biognosis is to offer any help in synthesizing materials, it is clear from the record that the experts have not found it. Very recently my colleague, R. E. Newnham (60), has ingeniously learned from the grunts generated in fish bladders, and the sound receiving systems of bats, to design and prepare successful composite transducers utilizing the same principles. These are the only **biognostic** derived “electronic” materials known to us. **Biomimetics** as a major design route for useful materials is not likely to be of significance outside of biomaterials, and excepting for White’s work (op. cit.) has yet to record its first success.

SUCCESS STORIES: I. LANXIDE

The history of the development of the directed metal oxidation process by the Lanxide Corporation is one of the most interesting success stories of innovative materials synthesis. For the first time in human history a process involving a reaction of $\text{Liq} + \text{vapor} \rightarrow \text{solid}$ was used to make useful materials. The ceramic matrix composites produced were the largest, simplest to make, and had many unique properties. The degree of innovativeness of the discovery can be judged by the fact that the corporation has filed nearly 3,000 patents worldwide in about six years and most are issuing with little or no challenge. Yet more than five years after the public announcements of the process (61-63) it is an extraordinary phenomenon that no more than one or two other groups in the entire world seem to have embarked on research in this process. Why? The only sharp difference from other fields such as high T_c superconductors, cold fusion, quasi-crystals, Buckyballs, is the **total** absence of deliberate publicity in the science press or newspapers since the company did not want such.

Table 4 shows the range of compositions of metal, ceramics, and reinforcements which can be incorporated into Lanxide composites. Table 5 shows some of the properties attained in some of these CMC. The second generation development by Lanxide of the metal matrix composites also made by this method, bodes well for directed liquid metal oxidation one of the most significant single synthesis and processing discoveries of the post-war era.

Table 4. Examples of Lanxide™ ceramic matrix systems.

Parent Metal	Reaction Product
Aluminum	Oxide, nitride, boride, titanate
Silicon	Nitride, boride, carbide
Titanium	Nitride, boride, carbide
Zirconium	Nitride, boride, carbide
Hafnium	Boride, carbide
Tin	Oxide
Lanthanum	Boride

Table 5. Nicalon™/Al₂O₃ mechanical properties.

Temperature °C (°F)	Flexural Strength MPa (k.s.i.)	Fracture Toughness MPa√m (k.s.i.√in.)
R.T.	461 ± 28 (8) (67)	27.8 ± 4.6 (3) (25.3)
1200 (2192)	488 ± 22 (12) (71)	23.3 ± 2.7 (3) (21.2)
1300 (2372)	400 ± 12 (4) (58)	19.2 ± 2.8 (3) (17.5)
1400 (2552)	340 ± 11 (4) (49)	15.6 ± 3.7 (3) (14.2)

SUCCESS STORIES: II. NANOCOMPOSITES: A MAJOR FUTURE ROLE IN SYNTHESIS

In the section above I referred to the real success story found in the chemical reactivity of nanocomposite powders themselves or when used as starting materials. This nanocomposite principle can be carried to the next hierarchical level of structure.

My argument above has been that we cannot purposively design new phases at the unit cell level. At the same time we have learned to design a whole world of composite materials. Initially the only application was for superior mechanical properties. In the 1950-80 period, a strong iterative process between technology and society has led to a more or less routinized capability to "synthesize" novel composites for structural uses.

However, the design of microcomposites for electrical, magnetic and optical properties was decades behind. While every semiconductor device is today a precisely architected composite, the different elements of the composite are used for their different properties. They do not interact to

enhance one property. In the last decade L. E. Cross and R. E. Newnham have designed from first principles and created whole families of electroceramic composites. These have been model examples of very fruitful T.T. research for over 15 years. The properties of such composites, e.g. the pioneering polymer-PZT transducer are often orders of magnitude better than the separate components. The paper by Newnham (64) provides a magisterial overview of the state of this art and gives the theoretical basis for this new thrust. It shows clearly why the future of synthesis will belong to such micro-nano-composites in the near-term future. Although no other families of applications have been analyzed and treated so thoroughly, similar composite materials are now appearing in magnetic powders and optical intercalates (65).

LOOKING AHEAD IN CERAMIC SYNTHESIS RESEARCH

Some time ago C. F. von Weizsacker, the physicist-philosopher, made the case (66) that thermodynamics was not symmetrical with respect to time. We cannot extrapolate from the past into the future even in fundamental physics. Prognostication must be based on the past record and any known constraints in the future. I have made the case (67) following Victor Weisskopf of MIT and Gunther Stent of Caltech, that useful and utilizable overall fundamental "scientific knowledge" is finite and that humankind is rapidly approaching the asymptote. Recently David Mermin (68) has made a more radical case that little new fundamental physics has been discovered since quantum mechanics.

What do I foresee in the field of materials synthesis and processing which has suddenly been singled out for policy attention in the U.S.? First one must exclude the absolutely certain flux of serendipitous discoveries from any analysis. However, the distribution of the flux, number and significance of serendipitous events may not be compared to the number and size of meteorites striking the moon or earth, because scientists are more like beachcombers going over already well-combed beaches. Moreover, contrary to glib assertions about the great value of new analytical tools and new computer capabilities, these are of little use and almost certainly will prove to be of negative value in really new syntheses. The major recent "discoveries": 1:2:3 superconductors, the diamond films, Lanxide, Buckyballs, putative cold-fusion required only the most modest apparatus available in most laboratories a century ago. Large instruments have historically proved to be idea-sinks, not idea sources. Of course, second generation materials engineering by, say, MBE machines, will be valuable.

The two spectacular successes in materials synthesis of the postwar era were the introduction of two active classes of materials: semiconductors and polymers. These step functions can never be repeated in scientific or technological significance. There are no more classes of materials left. The next set of discoveries will involve replacements of existing materials by others with superior performance. In the field of ceramics, since WW II, we have had entire industries such as the magnetic ceramic materials from the spinels to the garnets to SmCO_5 and the NdFe borides; the BaTiO_3 and PZT

capacitor and transducers, the various phosphors, the zeolite and other catalysts, and the optical fibers as the volume and dollar leaders. The field is much more crowded now, so that entirely new materials for new functions are doubly unlikely, and replacing an existing material is technologically very difficult indeed.

Hence in looking ahead one has to be very careful to analyze the impact of the new data one presents. In this connection, I will contrast two documents on the past and future of materials technology. The U.S. National Academies produced, after four years of committee work, the *Materials Science and Engineering Report* (69). In this report, we find a set of graphs depicting the enormous program which has been made in the improvement of the desirable properties of materials by serendipitous discovery or science-based engineering. Figure 14 shows four examples from superconductors, magnetic materials, etc. But a study of these figures forces one to a very important conclusion about future materials synthesis research: It has a very short life expectancy. In 1979 in my book *Experimenting with Truth* (67), I first made the case that these "exploding exponentials" guaranteed a very major change in a very short time (<25 years). Obviously if research on high T_c superconductors continues to increase the T_c at the same rate as in the past we will be above the melting point of all materials soon. Similarly the $B \times H$ product in magnets will be infinite, etc. The optimistic upbeat suggestion of the great advances we have made in this report, is therefore totally unjustified in their future scenario which would be roughly: If we keep going at this pace there will be nothing left to discover in 20 years.

Turning to the other document (30) from the U.K., Professor A. Kelly looks at the utilization of bulk materials. Figure 15 reproduces some of his figures. Here are plotted the total world usage figures for all the major metals and a per-capita usage of steel. These data present a very different tone for any planner. They tell us that humankind is reaching a new and unexpected asymptote in the total consumption of materials. That with more and more producers the battle for "market share" will increase. Part of the slowdown is due to conservation and an understanding of the finitude of resources. This "sustainability" argument is in fact slowly come to dominate technological decisions. Agriculture research dominated for nearly 100 years by growth scenarios and the research and technologies derivative of those (supported unquestioningly by all university and agriculture colleges) now finds itself radically re-directed towards low-input sustainable agriculture. Moreover it is instructive to note that this revolution did not come from a university or major industry. Instead it was championed by a few individuals such as Robert Rodale, the CEO of the Rodale Press, and Lester Brown, President of Worldwatch Institute. Another societal impact example is the fact is that in spite of the exaggerations both by the activists, and the apple industry, Alar is off the market and the apple industry is healthy—but again it was not done by the traditional research groups. **What is instructive from those snapshots on current R/D trends is that societal and environmental concerns have totally reshaped the research directions and agenda of agriculture research.**

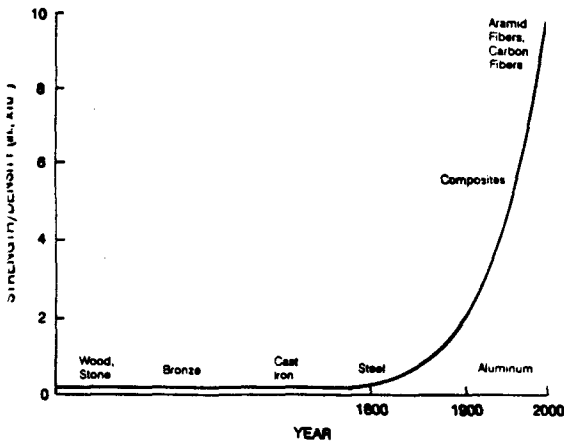


FIGURE 1.1 Progress in materials strength-to-density ratio as a function of time, showing 50-fold increase in the strength of today's advanced materials compared to that of primitive materials.

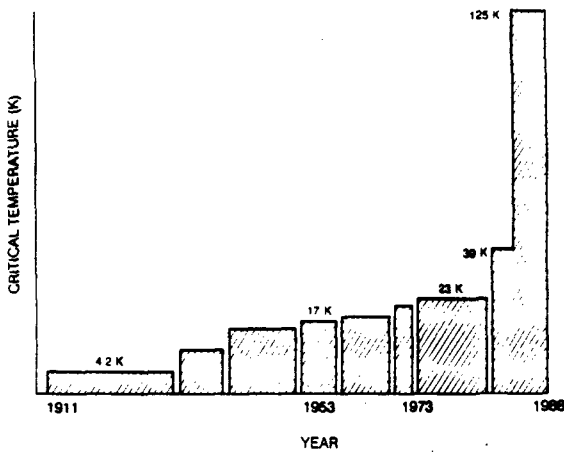


FIGURE 1.4 Progress of critical temperature of the best superconducting material as a function of time.

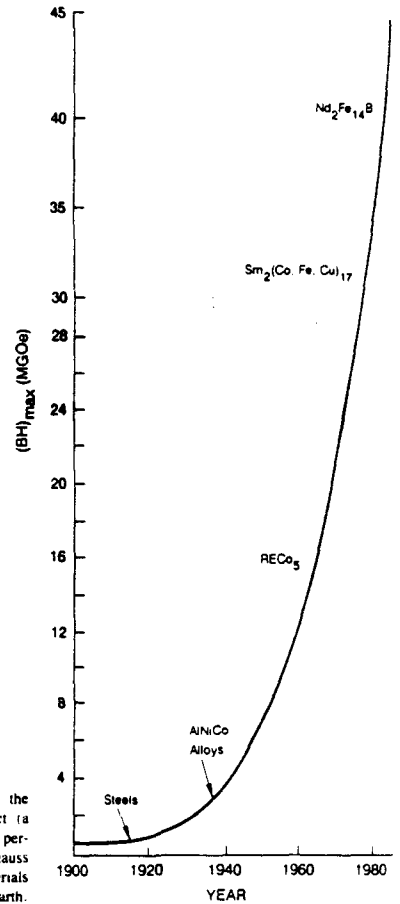


FIGURE 1.3 Progress in the flux-magnetization product (a measure of the strength of a permanent magnet in megagauss oersteds) of magnetic materials over time. Note: RE, rare earth.

Figure 14. Curves from MSE study by U.S. N.R.C. suggest that in a very short time we will have reached physical limits in property improvement.

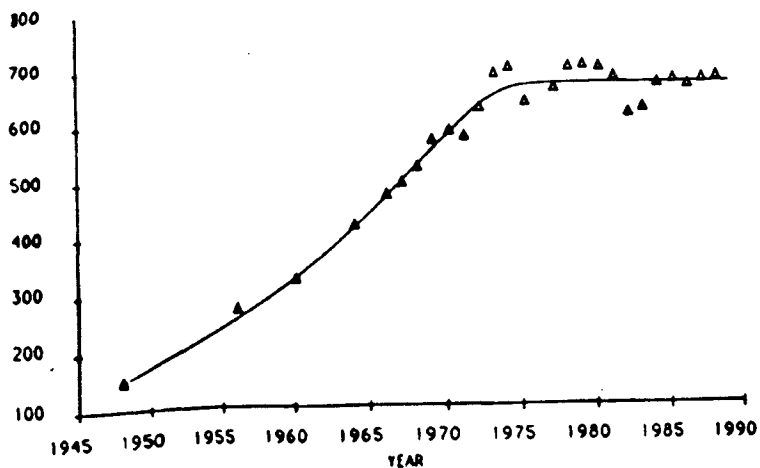
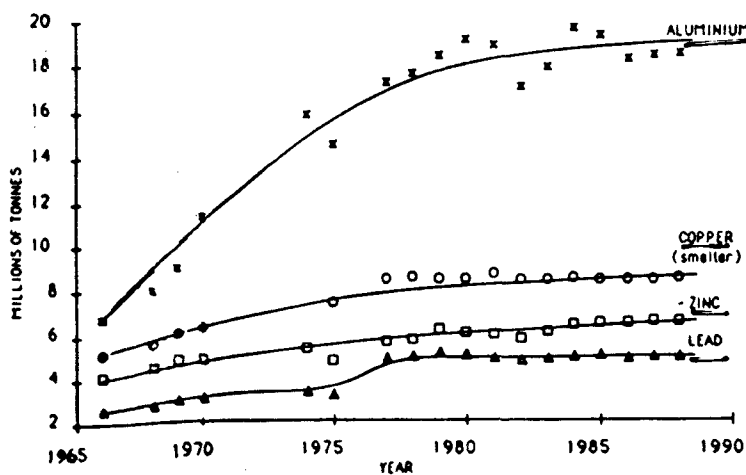
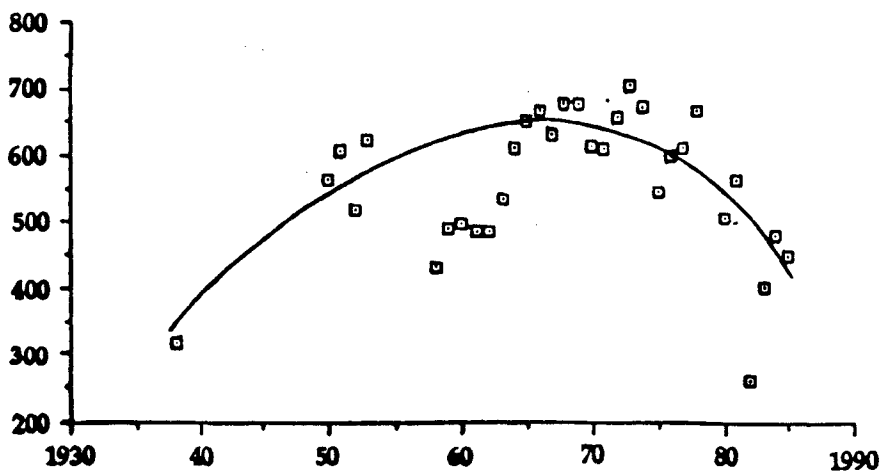


Figure 15. The future (1975-90) was obviously not predictable from the past (1950-75). World usage of all major classes of metals has plateaued after 1975. Per capita use is declining (after A. Kelly).

It is certain that analogous societal pressures—whether they are scientifically “correct,” or justifiable—will shape the future macro directions of *materials* research. It behooves the science community to anticipate such changes and start to reshape the directions of our research to match society’s new priorities. In “looking ahead” I see a radical change from the situation in the last 25 years. In the past whatever was discovered by the science community’s research set the directions for development and technology and thence the agenda for society. There was no countervailing force. That force has now appeared in the shape of the environmental demands of citizens translated into regulation by legislatures. It has appeared in the form of safety and “hypersafety” demands by the public. Hence the future research directions will be the resultant vector of one arising from societal constraints and the other from scientific discovery. I will end by treating each of these in turn.

Some Likely Directions for Discovery-Led Materials Synthesis Research

One cannot conceive of any materials developments which will come close to the enormous impact which the discovery and exploitation of semiconductors and of polymers has had on the materials industry. The functions which these new materials opened up in the communications and computer industries are now being fulfilled by third and fourth generation optimizations. Any new material will either be a drop-in improvement over the established ones—such as diamond over GaAs—or it will have a very hard time getting into the field. New functions for known materials based on new synthesis or processing will also have to compete against the existing technologies which are also constantly being improved. Twenty years ago the hope for ceramic turbines was very high. After enormous research expenditures the total role of ceramics in the engine area is now seen as being more modest.

On the other hand, the electroceramic area which was not much publicized has grown into a major industry. The high band gap and narrow gap materials are getting closer because of two advances in synthesis/processing. First the ability to make, say, diamonds and/or ferroelectrics, as thin films to mate with traditional semiconductor processing. Second, the switching from electronics to optonics involves a whole new range of electro-optical materials most of which are transparent, and this will make the way for more ceramic involvement in the communications technologies.

Table 6 lists the families of “bulk” and thin film materials in which I believe the successful research drive will generate some new opportunities. The family of “chemically bonded ceramics” as I named cement and its congeners, will offer continuing opportunities because these materials are needed worldwide for highways, buildings, waste disposal, i.e. for the entire population. And because these resources are geographically relatively uniformly distributed.

I have separated out the thin film form of ceramics as a special case because there is so far very little usage in this form, and hence specially attractive opportunities may present themselves. Just as metals have been widely used as a plated (or evaporated) thin film for electrical or chemical

applications, there appears to be no reason why ceramic phases and functionally graded materials may not make a major contribution here. The fact that ferroelectrics in thin film form are different from the bulk, and in fact one can modify the surface to change its properties, points the kind of direction where there will be many opportunities for research.

Table 6. New ceramic materials.

(a)	New (Bulk) Ceramics (via New Processes) <ul style="list-style-type: none"> • Functionally gradient materials • Lanxide as prototype of CMC • Chemically bonded ceramics (cements, clays, zeolites and other low temperature reaction products) • Nano-micro composites as substitutes in many fields
(b)	Ceramics in Thin Film Form <ul style="list-style-type: none"> • Ultrahard and/or conducting coatings <ul style="list-style-type: none"> – diamond, cBN, DLC, ceramic metals • Ferroic materials <ul style="list-style-type: none"> – active surface modified – passive: key properties different from bulk • Functionally gradient materials

Societal Constraints on the Future of Materials Synthesis Research

The basic societal trends are not difficult to summarize and I have attempted to do this in tabular form in Table 7.

Table 7. The future: Asymptotes and limits of low input materials-inventive technology. (LIMIT is analogous to LISA in agriculture.)

-
- Minimize energy and materials usage.
 - Minimize depredations on environment.
 - Cope with absolute physical limites.
 - Atomic scale inventions will continue to be serendipitous.
 - Nanocomposites is the major opportunity for new materials.
 - U.S. role in materials research will diminish rapidly.
 - New high volume materials will be driven by needs of less industrialized countries.
-

In the developed world, energy and materials conservation and environmental issues will dominate R&D directions more than property improvements. Many of these improvements—as indicated earlier—are coming up against absolute physical limits in any case. This is similar to the communications industry where transmission speed and “useful” information (for the masses) have saturated.

Really new materials will appear from time to time as a result of serendipitous discovery, but the commercial significance of such discoveries will inexorably diminish because existing materials are not going to disappear. No new laws of physics can appear to explain most of what humans do and experience (i.e. of any significance to other sciences or society, for the simple reason that the laws of motion, of electromagnetism, of quantum mechanics, etc., are so completely verified and adequate. So also the major classes of materials are established and they have been optimized for a myriad applications. Of course, each application driven by the commercial and social factors will seek to improve on the present materials, in a technology traction mode. It is in these applications where I see the emphasis on tailored micro and nanocomposites as playing the central role in materials synthesis in the decades ahead. Furthermore, as the U.S. role in materials research and in most science diminishes the science-push model will be displaced—indeed it already has been as witness the existence of the thrust towards synthesis and processing—by the technology traction model which is central to Japanese R/D management. The extent to which this has occurred is evident from Fig. 16, after Roy and Silsbee,

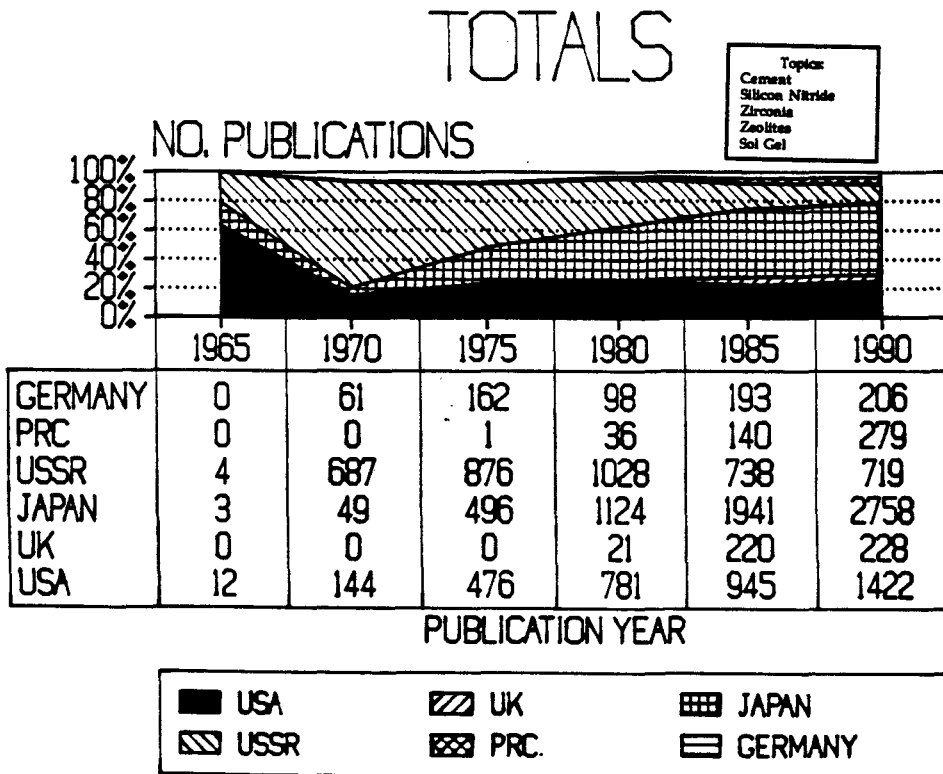


Figure 16.

(unpublished) which shows the dominance of Japan in published American research. The emergence of second and third tier countries as substantial research centers will also slowly move the center of gravity of materials research towards the basic needs of the vast majority of humankind in shelter, transportation, etc.

Changing Role of Research in Knowledge Management

A major change has occurred—unnoticed by most policy makers—in the value of locally carried out research in the total management of knowledge. Figure 17, taken from my presentation (70) at a conference on comparison of U.S. and Japanese research practice makes the following key points:

1. No local laboratory—even of the biggest industries—can produce more than a minuscule fraction of the total S^3 and S^1 discoveries being produced.
2. It is more cost effective by orders of magnitude to college knowledge (by carefully sifting through the literature, by visits to key laboratories, etc.) than to generate it.
3. That only experienced personnel in the S^2 -T.T. mode can find the most usable knowledge available and both put it to work directly and typically use it to guide the S^2 research.

What this implies is revolutionary in its implication for the training of scientists (that breadth of training and critical thinking are must more important than specialization). It is also revolutionary for research in third tier countries. Instead of investing in large specialized instruments they should invest in all major literature data bases and train managers to collect and sift new knowledge rather than generate it.

Goals for Materials Research in the 21st Century

Most humanists and social scientists have not accepted the classical model of “disinterested” (S^3) science. Moreover, the support of S^3 science, increasingly accurately perceived as a luxury “consumption good,” is certain to dwindle. The public will continue to demand more S^2 science. But can lofty goals be set for aspiring scientists in a partly globalized economy which on the one hand are sensitive to the new societal demands, and on the other encourage the inventiveness of the community? A recent Japanese document offers one such.

The Science and Technology Agency in Japan, in its February 1991 report to Prime Minister Kaifu, set as Japan’s R/D policy goal: “Harmony among science and technology, humankind and society.” In Fig. 18 I have combined this kind of universal goal for scientific research with the S.P., T.T., and M.P. motifs for research, expressing the clear change in the vector by which society will now drive and pull its needed technology and in turn its science (see Ref. 12).

KNOWLEDGE MANAGEMENT

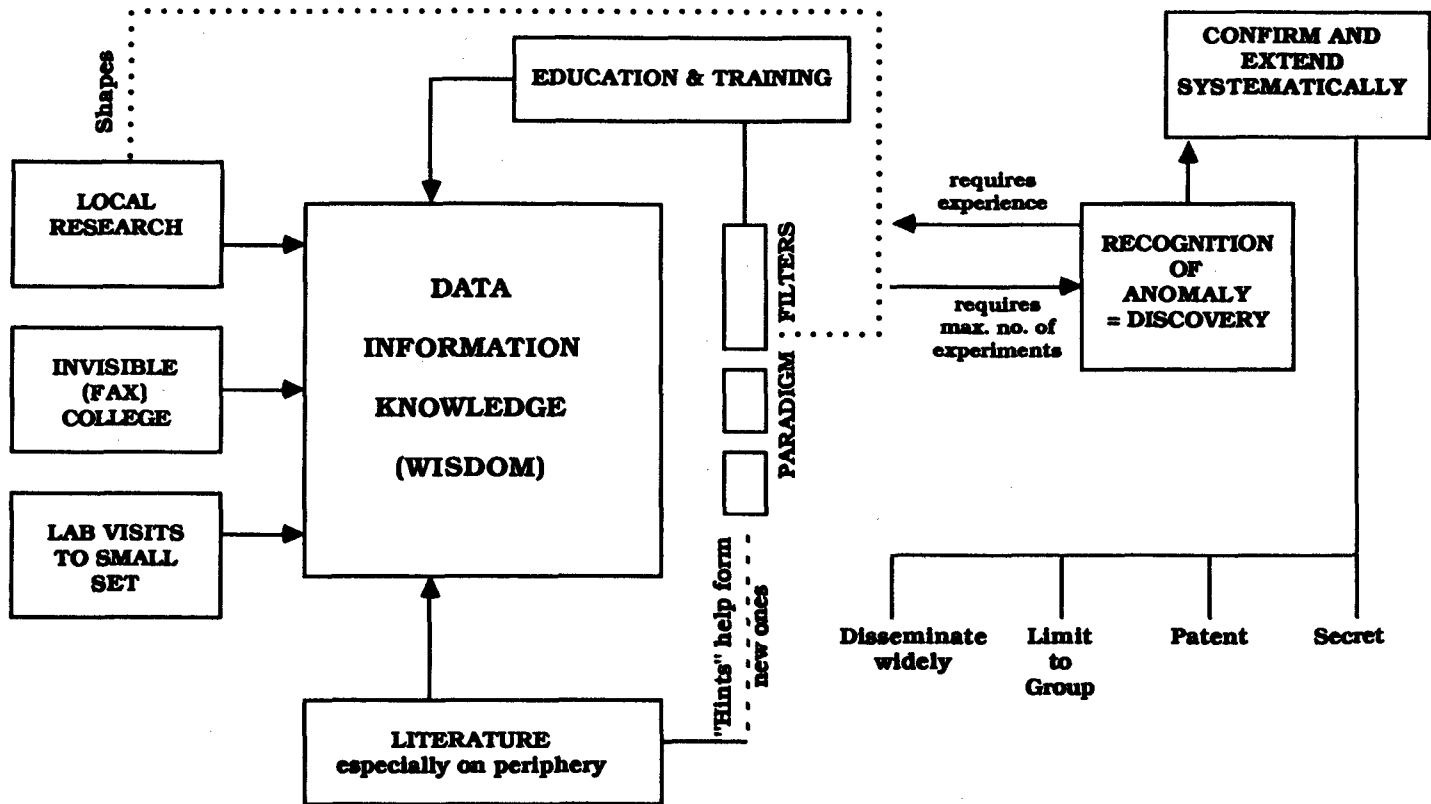


Figure 17. A new role for *local* research which radically diminishes significance is seen when it is placed in the context of the total flux of knowledge which universities or other agencies must learn to manage.

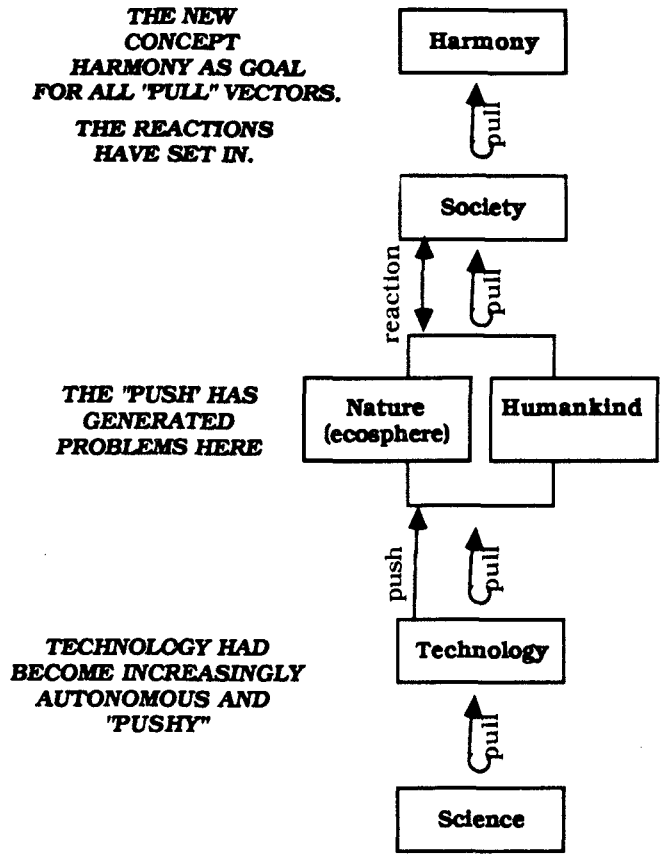


Figure 18.

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