

# New Materials

## A phenomenological exploration of the processes of research, development, and market diffusion

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### MARCHETTI-45

#### Resumé

*Materials are at the core of technological development through their mechanical, physical, and chemical properties. The approaching end of the Kondratiev cycle brings with it a flurry of innovations severely taxing R&D in materials with new exacting demands.*

Competition is harsh and in order to better invest inevitably limited R&D resources, a *taxonomic map* of what is going on can be of great strategic help. *This is what is attempted in the present study*, where R&D, measured in terms of publications and of patents over about 20 fields of material research shows very regular patterns. We have fitted them using a *diffusion model* derived from the Volterra-Lotka conceptual frame of biological competition.

Empirical observation over thousands of cases shows these diffusion processes to be very stable in time, lending the model with *robust predictive capacity*. Most of our results are reported here. They show the line of thought and the potential of the methodology for providing guidelines and rational support to R&D programs.

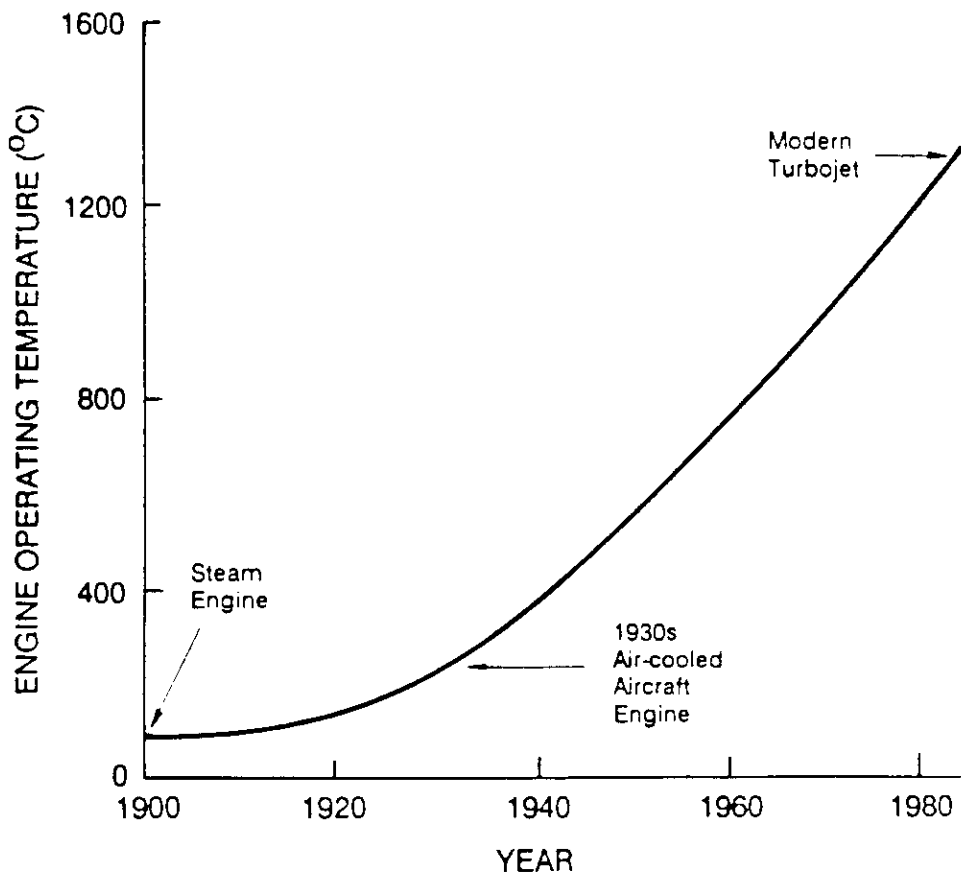
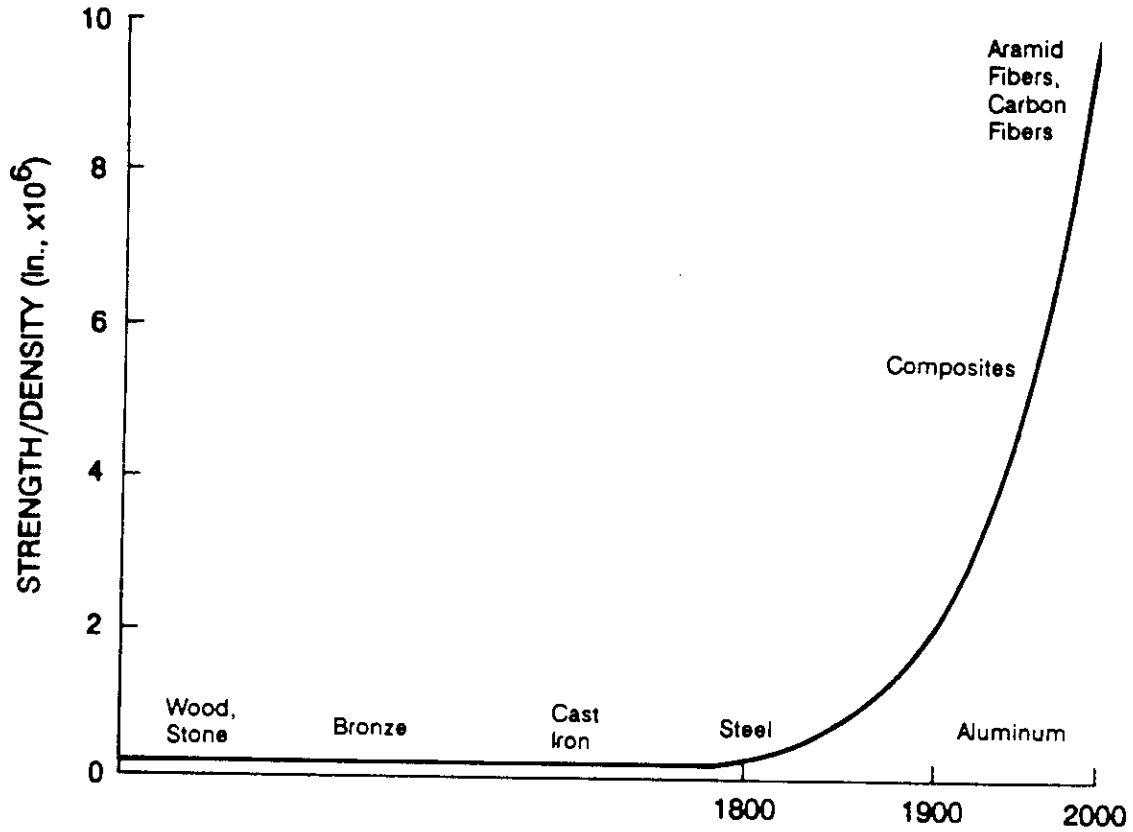
## Introduction

The mechanical and physical design of all sorts of machinery is quintessentially dependent on the physical and economic properties of materials embodying it. As a consequence high pressure has always been applied to materials developers. This is a standing demand and not really the consequence of the extreme sophistication of our technology. Iron was developed to provide an abundant supply of metal when bronze was technically superior but excessively expensive. Cheap iron was progressively developed to outperform expensive bronze, finally displacing it completely from the market, except for special niches, such as artistic casting, where molding and oxidation quality make it still still superior. Or for bells, where the low internal friction of the metal was put to use for musical purposes. Or for water and steam fittings where elasticity and corrosion resistance made it unsubstitutable until the advent of stainless steels.

I report here the very classical bronze case because it is paradigmatic. The competition between old and new materials follows exactly the same lines, although the time constants for a full substitution in the central niche, with subpopulations left in ancillary niches, are nowadays much shorter than before, but not really almost instantaneous as researchers usually think.

Although research on materials went on since ever, the avalanche started recently and can easily be measured by the results shown graphically in the illustrations of the following page. "Light and strong" improved by almost two orders of magnitude with respect to materials around the century, and in a particular application of aircraft engines materials now operate well above 1000°C.

An old paradigm, popular in research circles, is that first comes basic research, then from this high level abstract source the waters



are derived to run applied research which finally flows into the big sea of the productive system. Historical analysis of interaction between science, technology, and industry shows a magnificent isolation between the three, with occasional and accidental contacts until the industrial development of the last century where technological R&D and industry became conversant. To have science entering directly into the game we had to wait for the Second World War with the Manhattan project.

However, if we go to analyze research as more or less pure endeavor, measured by the number of papers covering a certain subject defined by the appropriate keywords and we analyze R&D by a perhaps less appropriate but insubstitutable indicator, the number of patents covering the same subject, we find all sorts of mix-up. Publications can well precede or follow R&D, i.e., patents, breaking the time sequence which is a prerequisite for cause and effect.

In the present research I have adopted a tool, conceptual and mathematical, that was *never used before in this area*. The concept is that *society operates through imitation of successful paradigms*. Imitation is assumed to be a *diffusion process*. In all cases we have examined, a few thousands, the mathematics of the process appears to be that of a diffusion process. This is obviously not the absolute proof, but only an indication that we can use the idea with good confidence.

*Diffusion is an epidemic process* where the number of entrants cumulatively grows until the fields is somehow exhausted. Epidemics are described by *logistic equations* (Figures 1 and 2). That this formalism can be applied to research comes from previous explorations I have done analyzing the literature. Cumulative number of papers on the effect of CO<sub>2</sub> on climate (Figure 3) is given as a first example mimicking the real epidemics of the London Plague of Figure 1. The S-shape of the logistic is transformed in a straight line

by manipulating the ordinates (Fisher & Pry transform) as described in the Appendix.

The analysis shows that the extremely complex process of entering a certain area, convincing other people that it is important, funding and executing research, publishing it, can actually be reduced to a very simple function having only three parameters. The phenomenon can be characterized in terms of *time*, *rate*, and *dimension* by these three parameters. A simplification very useful for higher taxonomic analysis, and possible generalizations.

Under the same general keyword one can have more than one pulse of diffusion. Closer analysis shows that some new finding in the principles or in the applications, starts a new course of research. This basically means that one should add a specifier to the general keyword. Apart from this, research pulses are usually exhausted in a single go, which is logistic measuring the *cumulative* volume of research papers or R&D as it may be represented by patents.

Another characteristic of the social and economic world we have analyzed in much detail is its *quasi fractal structure*. The same type of analysis can be done at world level or at regional level, or at the level of more detailed keywords, e.g., *multinational companies*, always revealing the same basic structure of *nucleation*, *selection*, *diffusion*, if with different parameters in the equation.

In the present research I have systematically used the data bases of the Chemical Abstracts and of the American Ceramic Society because they have reasonably long time series and are very well organized. (Other sources have been employed especially for what concerns production quantities.)

From these abstracts I usually took the world references, with the argument that development of new materials is such a complex and worldwide operation that the best image can be gathered by looking at the world as a single object. However, some examples of subdivision by area are shown, e.g., for patents, to show the

validity of the fractal concept.

Zooming into the European Common Market area or the single nations, or the single industries is certainly possible, but it requires an effort in data gathering which is beyond the size and the scope of this contract which was intended to be *exploratory and methodological*.

## New Materials Considered

In the choice of the new materials to be taken into consideration I tried to strike a balance between the different objectives in the use of the materials themselves.

*SiN*, *Sialon*, *Metallic Glasses*, and *Thermotropic Liquid Crystals* represent the *structural uses*, referring to the very hard, the very tensile, and the very tough. Also inorganics, metals, and plastics are represented.

*GaAs*, *Conducting Polymers*, *Rare Earth-Cobalt Magnets*, *Optical Fibers*, represent the *functional uses*, where the electric, magnetic, and optical properties are the prize of the game. Again with inorganics, plastics, and metals.

At the level of patent analysis, *Advanced Composites* show the working of the model at a higher *aggregation* in terms of material specification, and at a certain *disaggregation* in terms of actors (Germany, Japan). For *Metallic Glasses* patents in the USA the analysis has been done in a much more detailed frame. First the *totals* of patent applications and of patents granted has been modeled, then the same analysis has been repeated by source country, taking as sources (USA), (J), (D), (EC).

Diffusion of a product, i.e., the amounts produced for each of the new materials in the study has been analyzed for a very few cases. The search for the quantities produced has been in fact

extremely elusive. The data are usually scattered, occasional, and unreliable. I think a *data collecting procedure* in this field could well constitute an *action by the Commission*, perhaps through or with the collaboration of the *Statistical Offices*. The knowledge of the quantities, as Maria Theresia well knew, is an instrument of planning and power. In our case it is more modestly a necessary prerequisite for *research and forecast*.

The *model certainly applies* to the diffusion of an innovation *in terms of number adopters and of quantities used*. That is in fact the field where we used it first. Some examples are reported for the specific case of new materials.

A last observation is about the statistics. The data listed by Chemical Abstracts or the American Ceramic Society, or by a manual counting of the literature, can never be complete. They have to be seen as a sampling and be reasonably sure the sampling is correct, i.e., loss of counts are evenly distributed. The electronic procedures of the above data bases insure coverage of a large number of journals. The same can be said for patents where all of the significant countries are included.

The model operates in relative terms, and the results are the same for samples of different size except obviously for the size of the sample. In other words, samples from different sources, but collected using the same criteria, should have the same central date, when e.g. research is growing at maximum speed, and the same rate of growth ( $\Delta T$ ). This number which represents the time to go from 10% to 90% of the saturation level has been taken as an intuitive proxy for the rate constant of the equations.

In the following pages each case will be presented and discussed separately. As a kind of sum-up I would say that the exploration went well. *The mutation selection diffusion approach and the associated mathematics, work unimpeachably in the fractal recesses of inventing, developing, and selling new materials. Because the*

*analysis is predictive it can provide a good basis for strategic planning.*

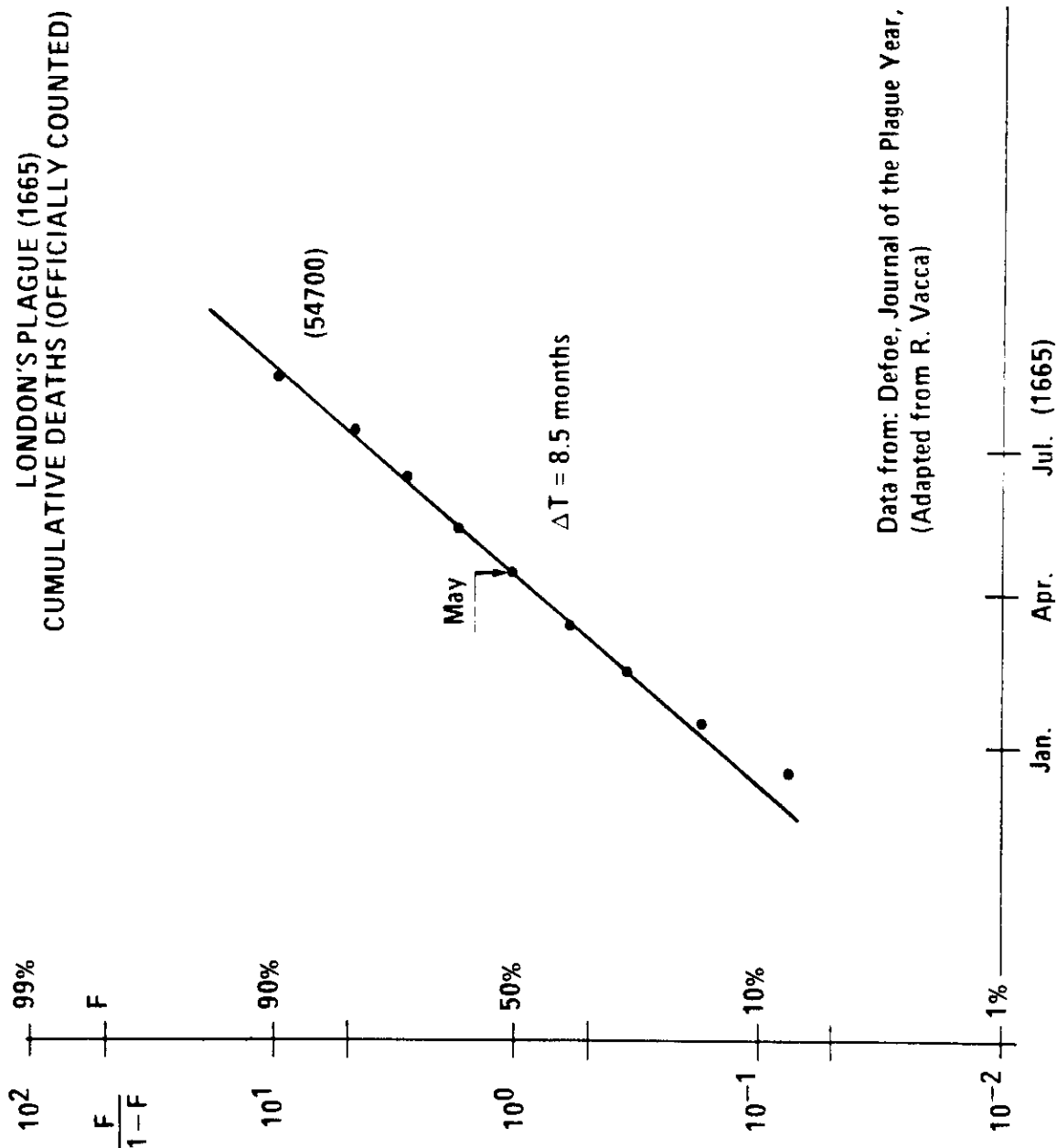
The observation of the time constants for the various cases shows, however, that they tend to be relatively short, mostly in the range of 5 to 10 years. This means organizational reflexes have to be fast, at least in bureaucratic terms. In clear terms 80% of the activity in each of these subjects is explicitated in periods of 10 to 20 years.

At this level of analysis our methodology does not permit the forecast of the starting of *new lines* of research. As shown in previous studies and on different subjects (e.g., energy or transportation), working on higher rank fractals can lead to quantitative statements on where the system is going, providing signals of alert for the proper areas.

We suggest that CEE takes the follow-up of this research on a permanent basis, putting as a first item on the list the creation of *statistical files (data banks) on all the subjects that might become of interest for the Community*. The work of analyzing them and providing on-line information for the *best definition and justification of medium-term R&D strategies* will be enormously simplified.



Figure 1.

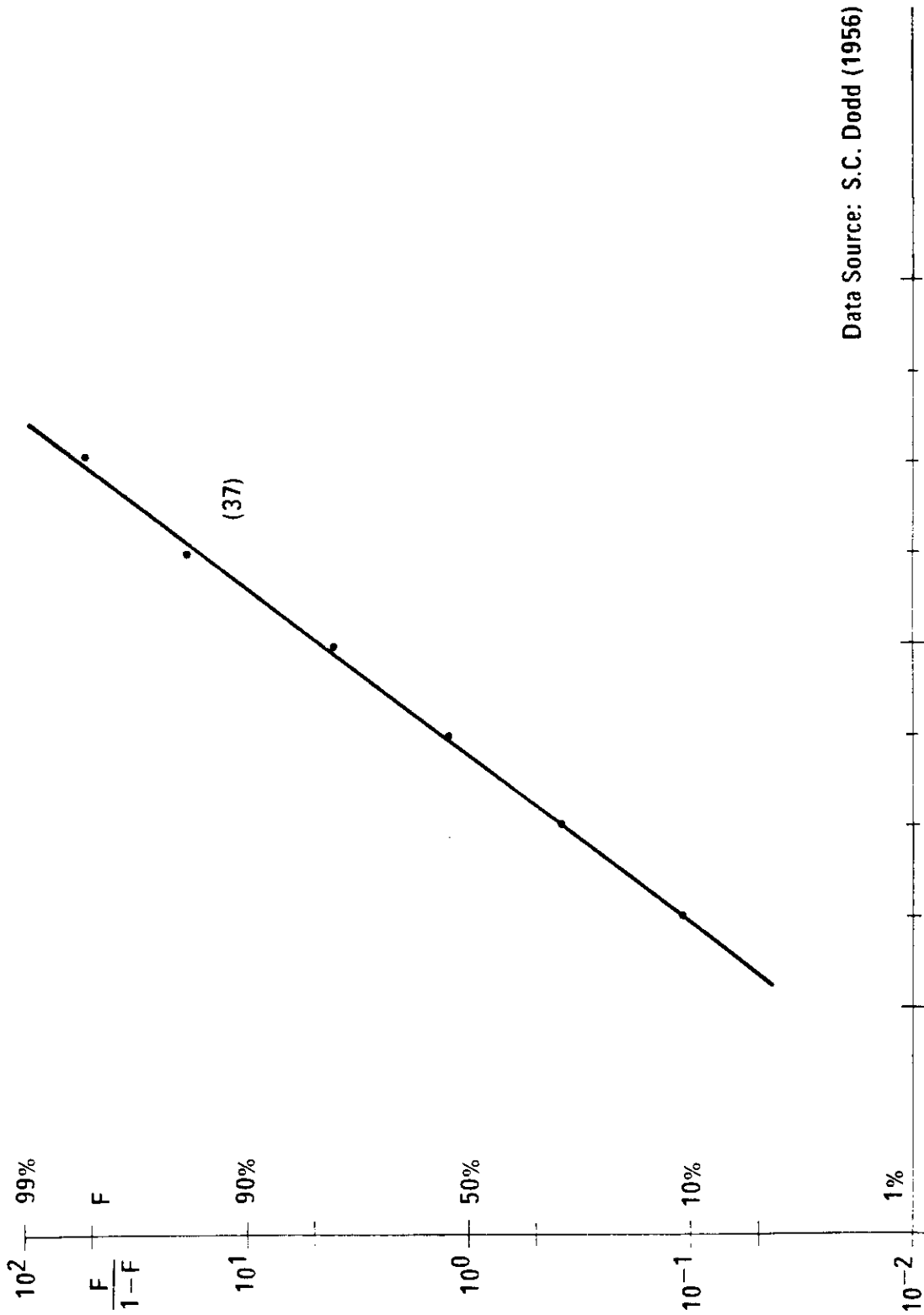


## Figure 1.

The epidemiological equation is tested here on a real epidemics measured through the proxy of cumulative number of deaths. The total number of deaths is given in parenthesis. This number can be calculated when the process is going by best fitting the diffusion equation to the data. It is called *the niche* in analogy with the carrying capacity of certain environment for a certain species. The growth of a biological species into its niche follows again a logistic equation.

Figure 2.

DIFFUSION OF MESSAGE IN BOYS CAMP POPULATION  
(42 BOYS)

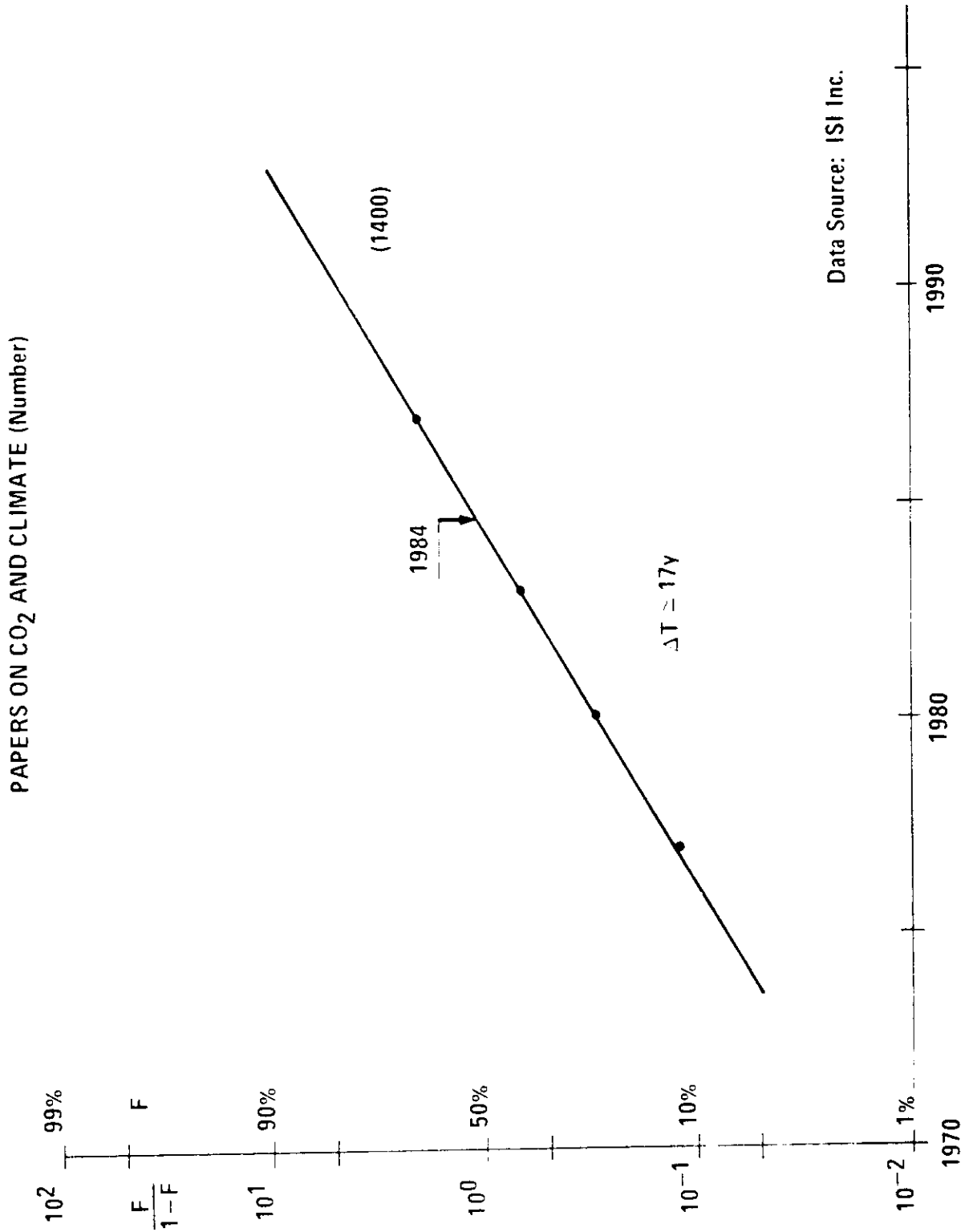


C. Marchetti, IIASA, 1988

## Figure 2.

Also messages diffuse epidemiologically, as shown by this experiment in a boys' camp. It is interesting to note that the saturation point, the final number of boys that the message will reach, is slightly lower than the actual number of boys illustrating the concept of niche and the existence of a separate small clan immune to social messages.

Figure 3.



Data Source: ISI Inc.

C. Marchetti, IIASA, 1988

### Figure 3.

Writing a paper on a certain subject is a very complex process. One has to get the appropriate stimulation, have the competences, find time and funding, identify a journal that will publish the results. The complex process can be reduced to the scheme of our epidemics, as shown here using as a proxy the final result, i.e., the cumulative number of papers published. The subject considered is the “effect of CO<sub>2</sub> on climate” and the analysis gives a crisp definition of the course of the “epidemic”. The date when papers publication was at its maximum is 1984. 90% of the papers or  $1400 \times 0.9 = 1260$  will already be published in  $1984 + (17:2) = 1993$ . This shows the fad has almost reached its exhaustion point and from a research strategy point of view it may be not worthwhile to invest into it. It may happen, however, that a new wave of research may start following some conceptual breakthrough in the area.

## Advanced Composites

Composite materials are an old idea in biological systems where fibers with certain physical properties are embedded in a matrix that provides the physical connectivity of the bundle. Composites have a long history in materials production and I can quote *Eternit* as an ancestor of the class. Advanced composites are the ones using the latest combinations, like carbon, boron or kevlar resins embedded in thermoset and thermoplastic resins. Their performance is usually measured in terms of strength/weight ratio.

Aeronautics and sport objects (boats) are usually the first target for marketing them. Their cost is not pegged higher for intrinsic reasons, so that their use may well spread in time into lower value market, as for car bodies. Similar things can be done using fibers and metal or ceramic matrices (Eternit!). In spite of being very tricky combinations, they are starting to find uses, e.g., boron fiber reinforced aluminium tubes are employed for Space-Shuttle structures, saving about 150 kg of weight per shuttle.

More down-to-earth applications are, e.g., in the wear surface of aluminium diesel engine pistons made by Toyota with aluminium reinforced by alumina-silica fibers. With 300.000 pistons/year this seems the largest application so far.

The automotive industry ordinarily does not use appreciable quantities of advanced materials, but uses very large quantities of engineering materials, in addition to vast quantities of commodity materials. It is an important user of aluminium alloys, microalloyed steels, polymers, PMCs, and ceramics, and a small but significant user of superalloys and titanium alloys. In the near future, the industry will probably become an important user of certain advanced materials, such as neodymium-iron-boron magnets and glass fiber wiring.

A final case of composites should be that of dispersions, e.g., of rubber droplets into plastics to make them less brittle and more resilient. Here some definitions are still necessary to split this case from that of alloys where often precipitates fulfill exactly the same function.

Patent applications for advanced composites in the USA are analyzed in Figures 4, 5, and 6, for totals, Germany, and Japan, respectively.



Figure 4.

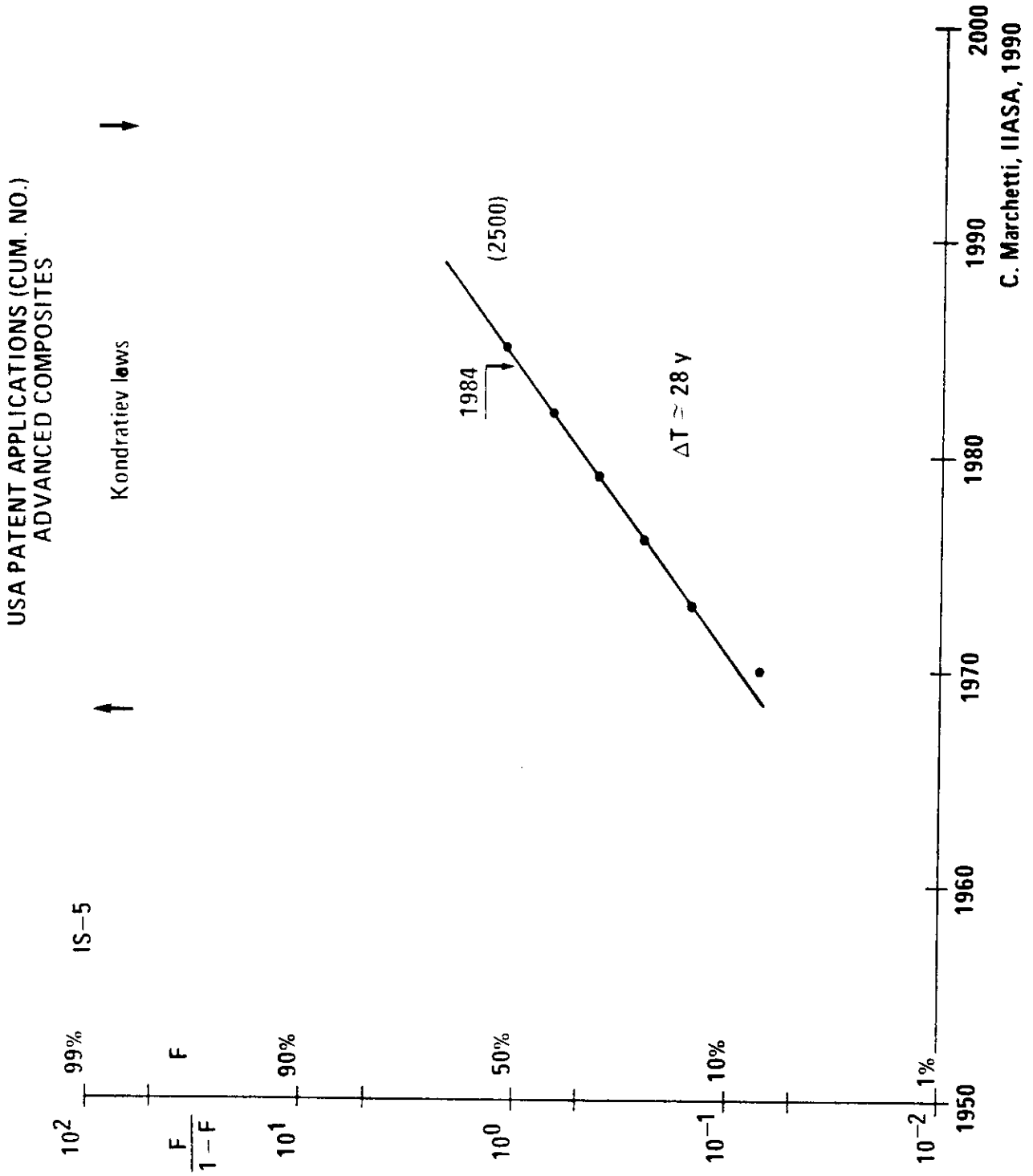


Figure 5.

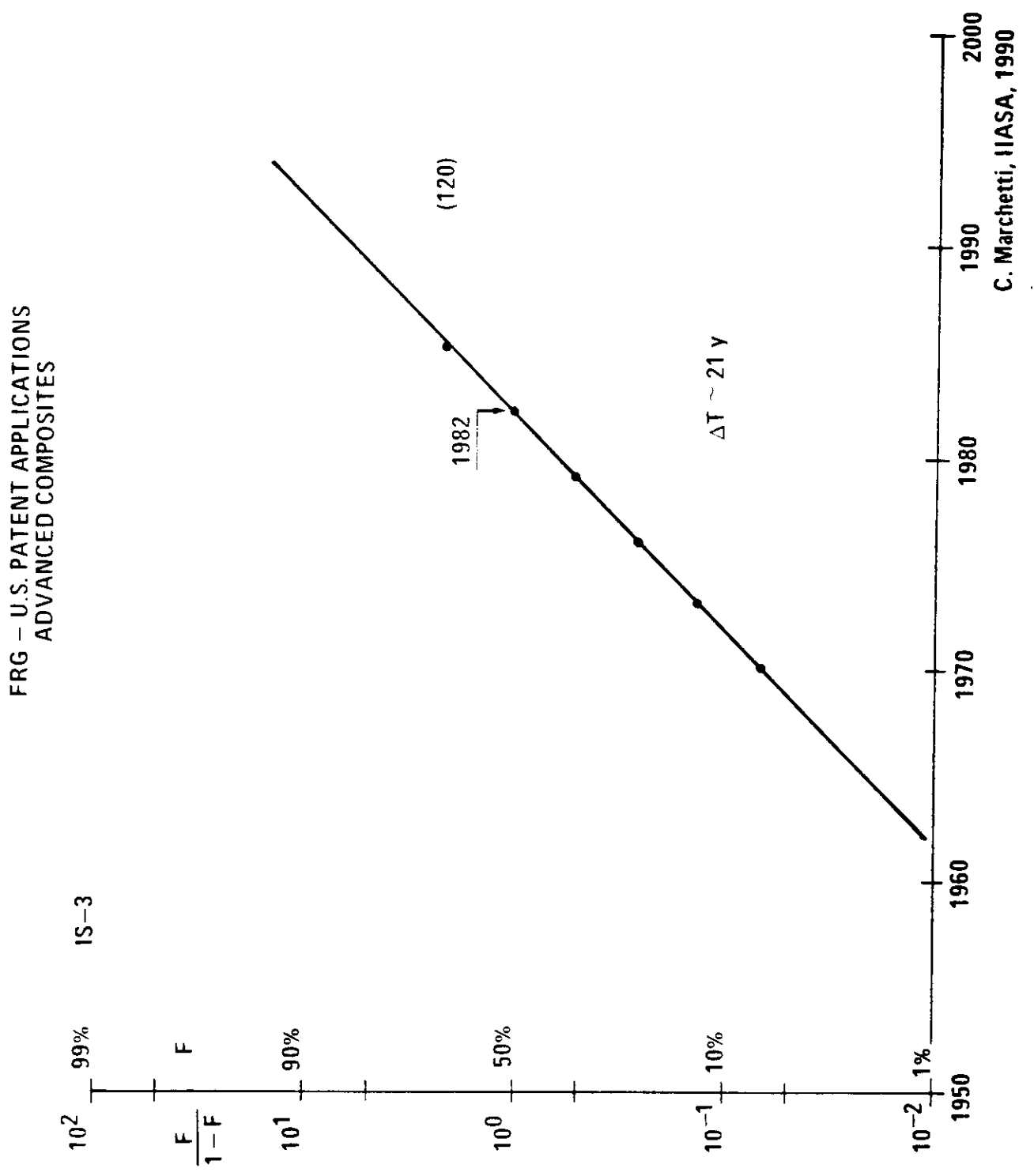
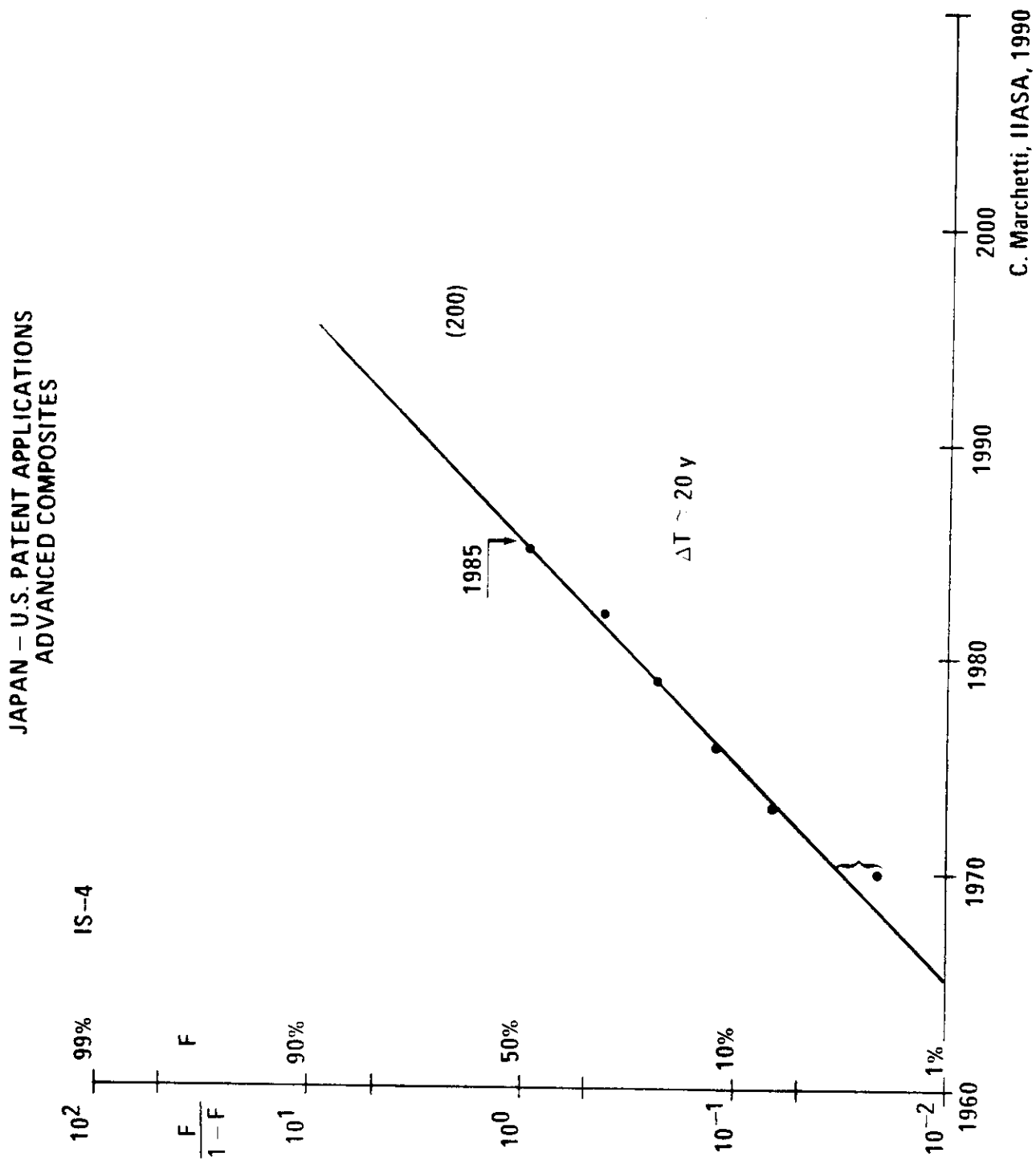


Figure 6.



### Figures 4, 5, 6.

Taking a generic keyword, *Advanced Composites* we can analyze *Patent applications in the USA*. The result is given in Fig.4 for the total number of applications. The time constant of 28 years shows the process has a total length (from 1% to 90% of saturation) similar to a Kondratiev cycle (55 years). In fact many economic phenomena are strongly modulated by the cycle. In this case however the centerpoint in 1984 would be fairly out of phase with the centerpoint of the cycle in 1968. R&D tends actually to intensify during the innovation period which occurs around the end of the cycle (1995). The analysis can be zoomed by looking at the contributions of Germany (Fig.5) and Japan (Fig.6) in terms of patents they have deposited in the USA. The FRG is relatively earlier (centerpoint three years before the mean) than Japan (centerpoint one year after the mean) but with a smaller number of entries (120 instead of 200).

## Metallic Glasses

Metallic glasses are a new playfield of solid-state physicists and metallurgists who were able to freeze an almost liquid state, by very fast cooling, of molten metals and alloys. The peculiar properties, mechanical, electric and magnetic, of these materials brought a flurry of proposals for their application in technology and a consequent rush to patent.

In conventional or ingot processing, the cooling rates from the liquid state are of the order of 1 K/s or less, and may be as small as  $10^{-3}$  K/s. The cooling rates in rapid solidification processing, however, may vary from  $10^2$  K/s to as high as  $10^8$  K/s. These rates are so high that thermally driven diffusive rearrangement of atoms during cooling is impeded or wholly prevented. Highly nonequilibrium structures are then produced, often with unique properties. At sufficiently high rates, many alloys can be produced with an amorphous, or glasslike, atomic structure. At somewhat slower but still quite high rates, very fine grained crystalline structures are obtained, often in composition regimes that are not accessible to conventional processing.

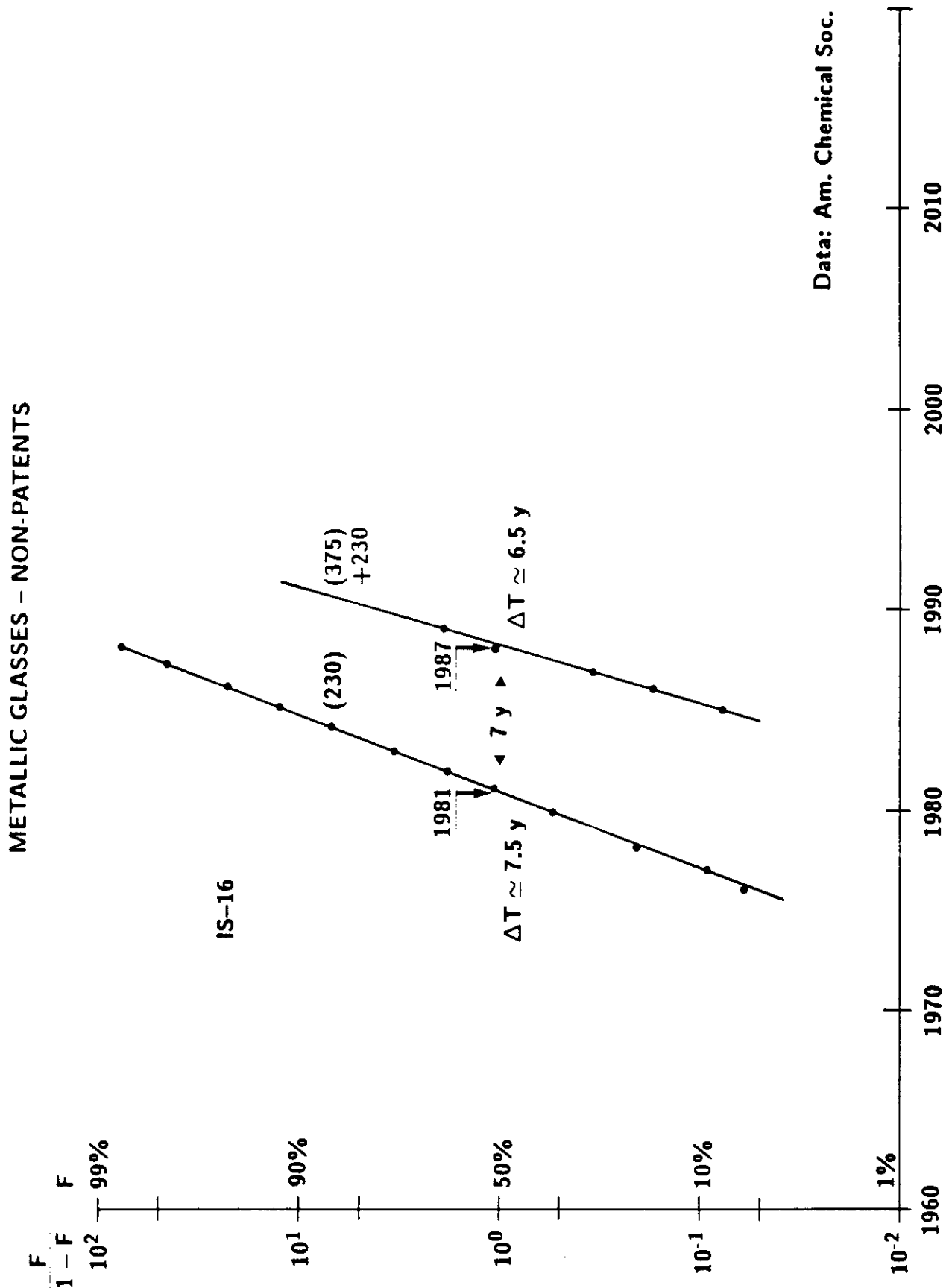
Rapid solidification technology has led to materials with new and useful combinations of magnetic properties. Attempts now under way to exploit their unique soft magnetic properties should lead to applications in electronics, power distribution, motors, and sensors. New permanent magnets recently produced by rapid solidification should be useful in building compact, powerful, electric motors.

Direct ribbon casting is a version of rapid solidification that has much promise for producing thin sheets of materials with unusual combinations of properties. Among the present applications where this technology has led to improved performance and lower costs is the production of brazing filler alloys, solder alloys for electronic packaging, and thin stainless steel sheet.

Rapid solidification also has been used to produce fine-grained and homogeneous crystalline – as opposed to amorphous – materials with much-improved properties and performance. The materials that have responded well to this processing technology include high-strength aluminium and magnesium alloys, tool steels of high toughness, and nickel-based superalloys.

Rapid solidification recently played a key role in the remarkable discovery of the so-called quasi-crystalline phases. These phases were first produced accidentally during rapid solidification of aluminium-manganese alloys. The scientific interest in these phases arises from the fact that they display long-range order – they are not amorphous or glassy – but the symmetry of the order is not consistent with the heretofore accepted rules defining the allowable symmetries of crystals.

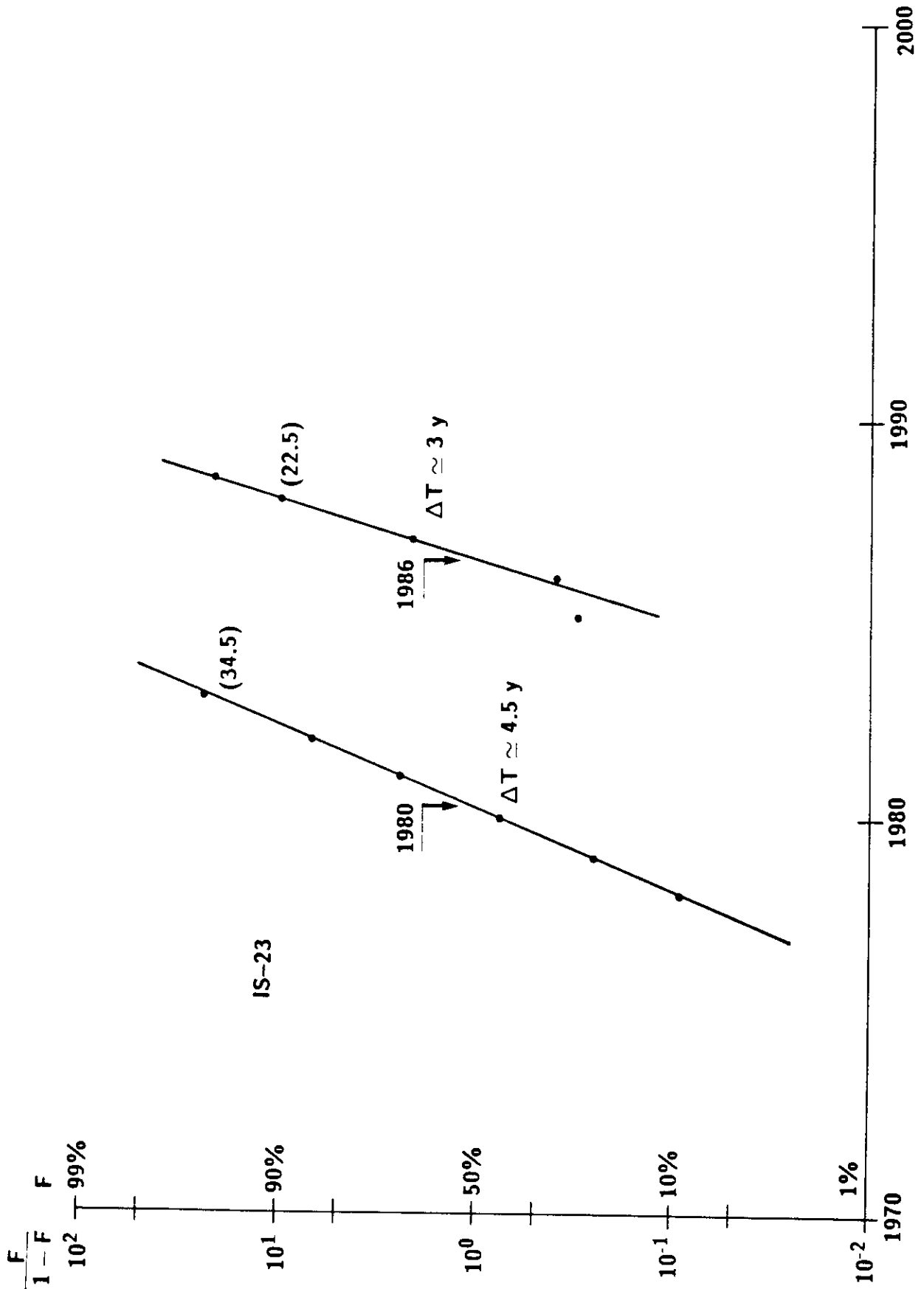
Figure 7.



C. Marchetti, IIASA, 1990

Figure 8.

METALLIC GLASSES - PUBLICATIONS



C. Marchetti, IIASA, 1990



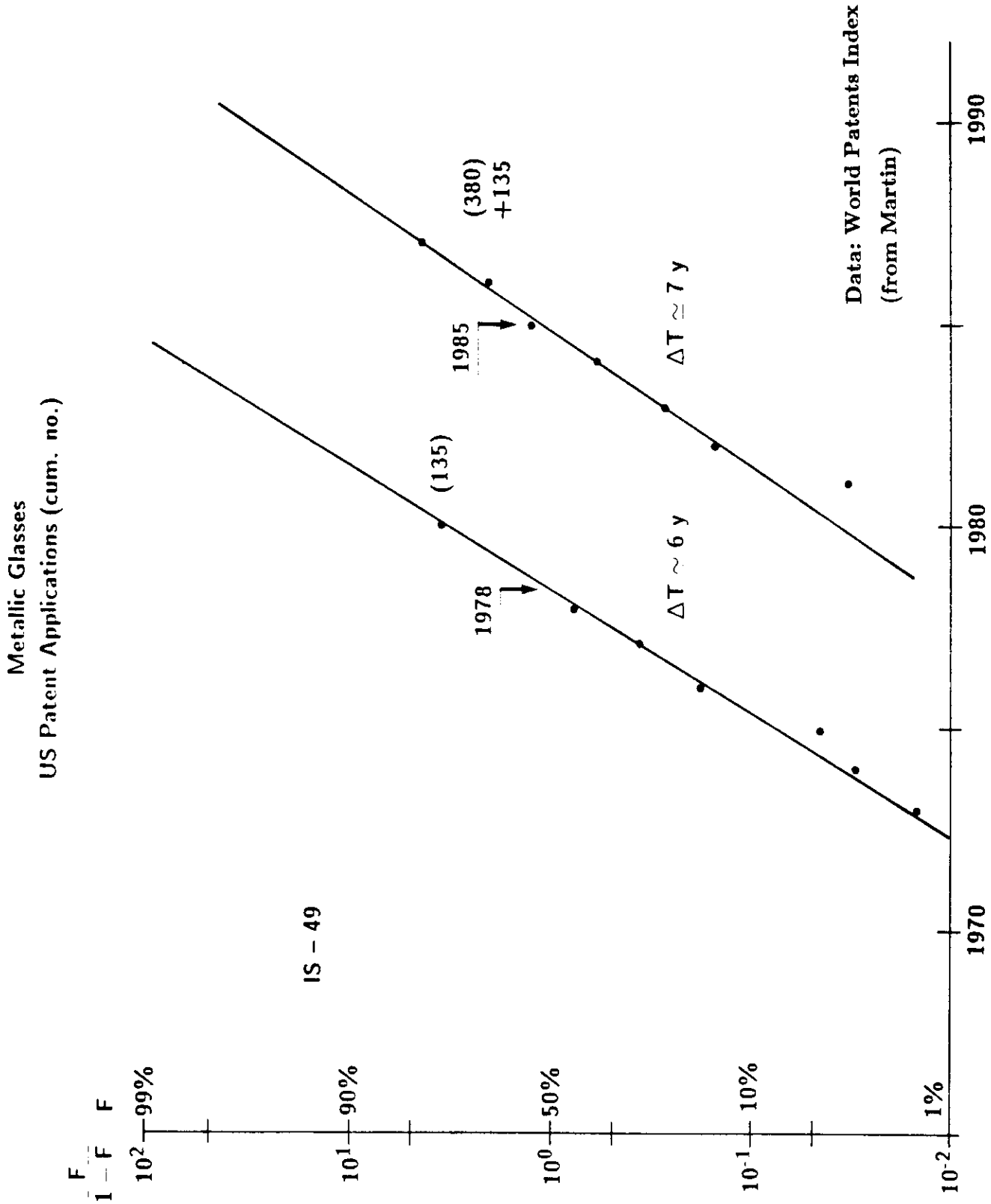
## Figures 7, 8.

The situations of publications worldwide on the subject of Metallic Glass, as reported by Chemical Abstracts and Ceramic Abstracts, are reported in the following, as the situation of patents in the USA as reported by the World Patent Index is analyzed in the following charts.

The publications reported by *Chemical Abstracts* are mapped in Fig.7. The two waves have their centerpoints in 1981 and in 1988 with 230 and 375 (at saturation) papers reported.

These lists depend on many factors, e.g., on the specific definition of the subject, and on the set of journals and patents scanned. For a comparison we have taken the publications listed under *Metallic Glasses* in *Ceramic Abstract*. The result of the exercise is reported in Fig.8. Although the number of objects is by an order of magnitude smaller than in the case of publications from *Chemical Abstracts*, the result has some important consistencies. The waves are two in both cases and their centerpoints differ by only one year for the first pulses, and by two years for the second. The pulses appear to be much sharper if seen through the *Ceramic Abstracts* compilations.

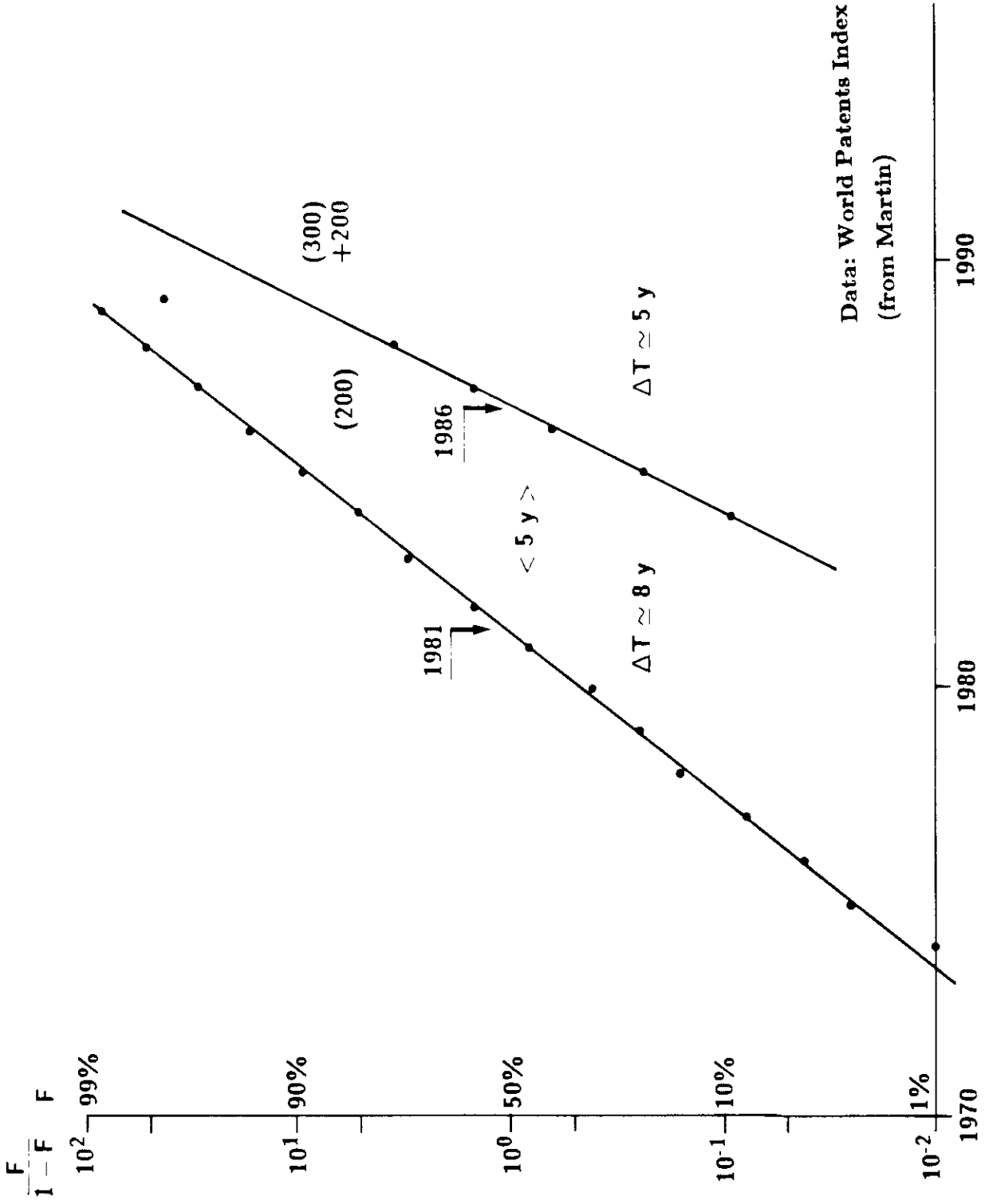
Figure 9.



C. Marchetti, IIASA, 1990

Figure 10.

METALLIC GLASSES  
US PATENTS PUBLISHED



Data: World Patents Index  
(from Martin)

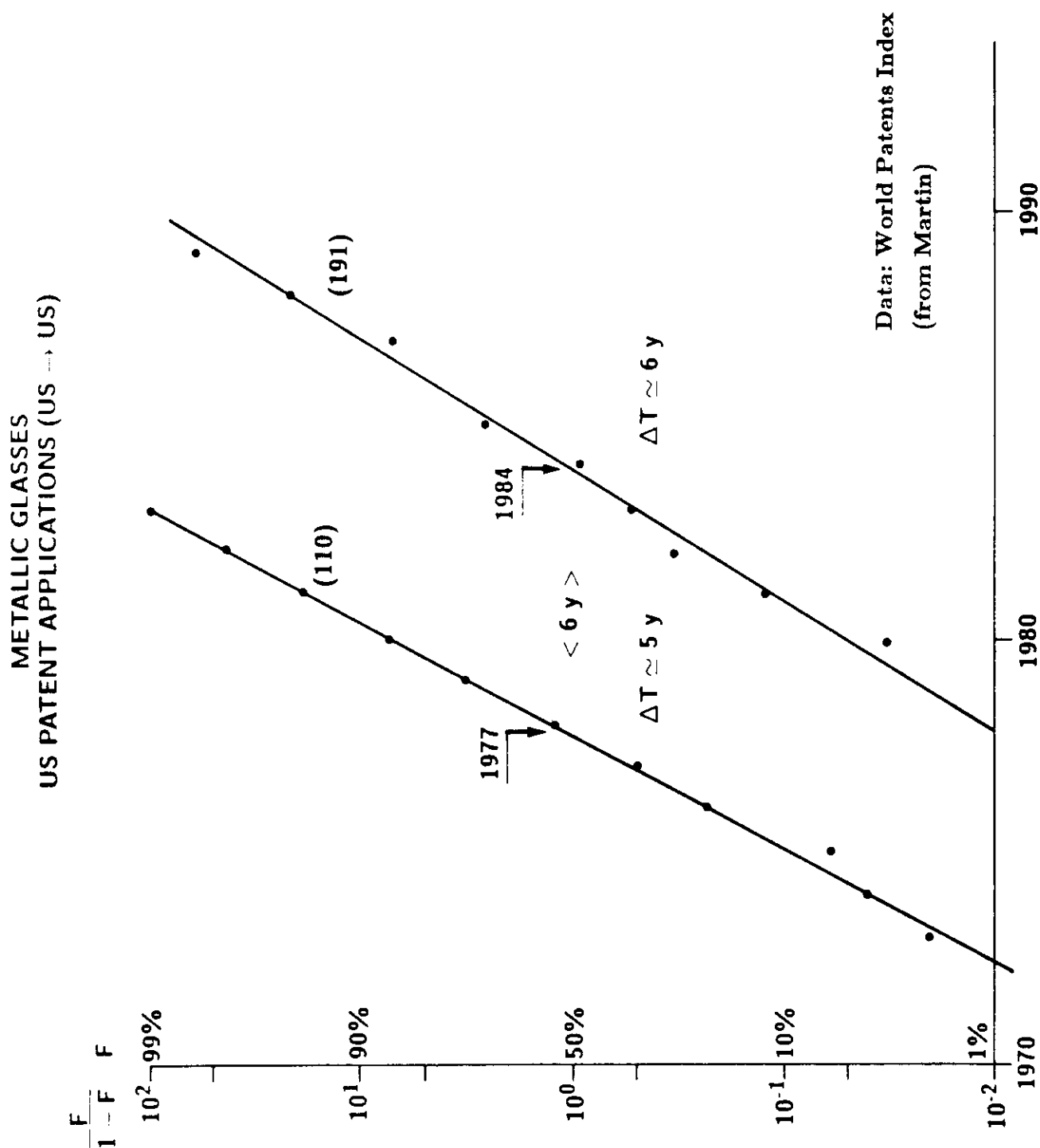
C. Marchetti, IIASA, 1991

## Figures 9, 10.

Patent applications in the USA (Fig.9) show again two pulses, but the first has a centerpoint in 1978 with a total of 135 patents applied for. This pulse has more or less the same time constant of the same time constant of the first publications pulse, but it *precedes* it by three years. The second publication pulse is centered in 1988 and follows patent applications.

The granting of the patents is reported in Fig.10. Again we have two waves, one centered in 1981, three years after the first wave of applications, and the second in 1986, just one year after the second wave of applications. the sets of application and granting of patents do not show a complete self-consistency, because for about 10% of the patents the World Patent Index listing did not give the application date. The methodology is powerful but great caution has always to be used in qualifying the data bases. There is always the danger of extracting wrong signals from wrong or distorted data sets.

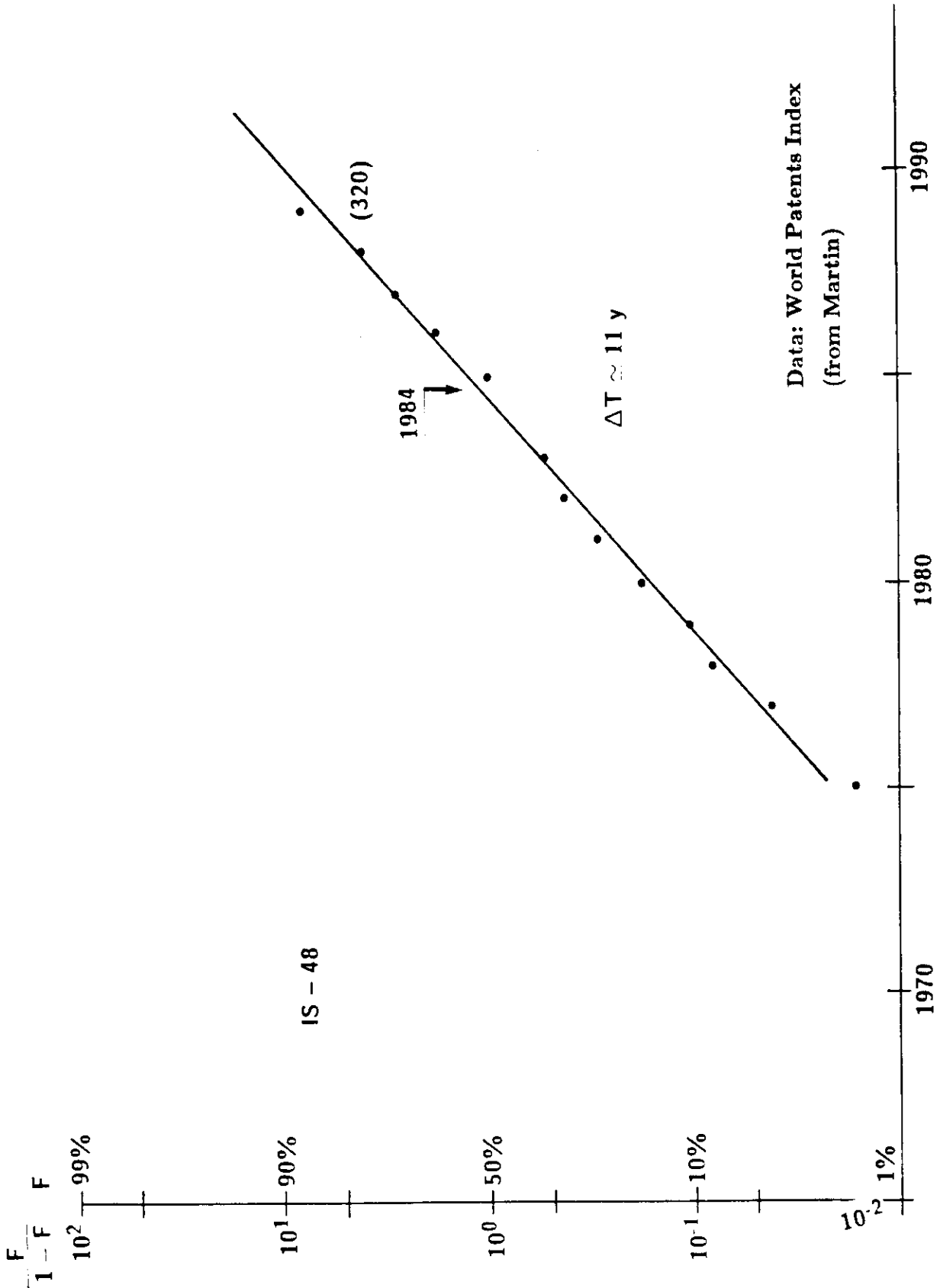
Figure 11.



C. Marchetti, IIASA, 1991

Figure 12.

Metallic Glasses  
 US Patents (US → US) cum. no.



C. Marchetti, IIASA, 1990

## Figures 11, 12.

One can zoom into the aggregated data of Figs. 9 and 10 and look for the contribution of various nations or groups of nations (EC). The first piece of disaggregation is given in Fig.11, where *patents originated in the USA* are analyzed. Again we have two waves, one centered in 1977 and the other in 1984. This shows some anticipation, if only by one year, by US patentees, with respect to the whole rush as represented in Fig.9. This does not mean Americans were first in the art of Metallic Glasses. Applications from other countries often follow the application in the land of origin. However, the World Patent Index permits a reconstruction of pathways and to build realistic rankings between nations or areas (EC).

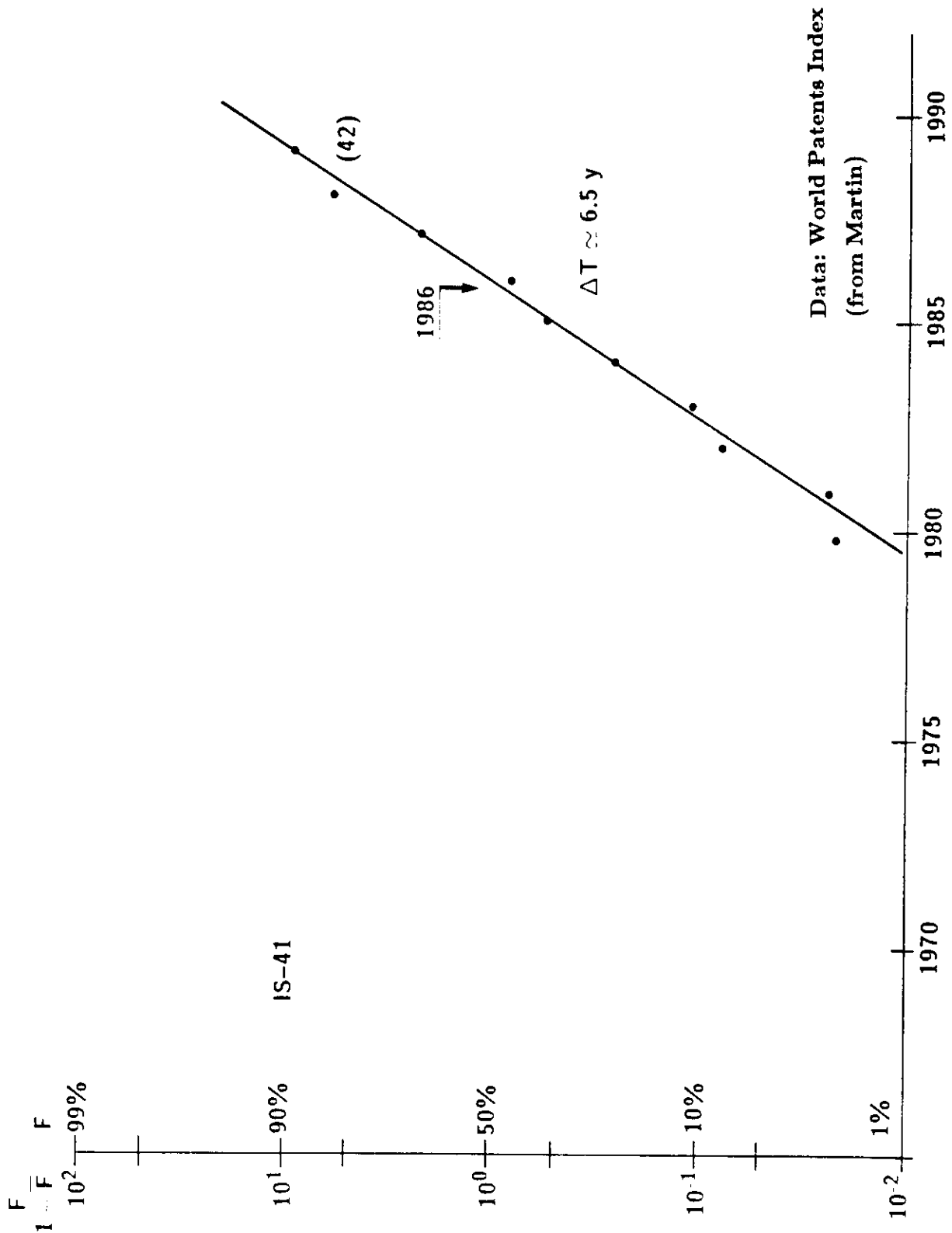
The granting of the patents (Fig.12) show a single go centered in 1984, although the irregularities around the fitting curve may suggest an attempt at splicing to get a better match.

	A	B	C	D	E	F	G	H	I	J
1										
2										
3	Country of origin for patents published in U.S. but with unspecified application date									
4										
5	PUBLICATION	YEAR	DE	FR	JP	US	NL	CH	GB	TOTALYR
6		1972		1						
7		1973								
8		1974								
9		1975								
10		1976			1					
11		1977								
12		1978			2					2
13		1979		1						1
14		1980			2					2
15		1981		3	2					5
16		1982		2	6		1			9
17		1983		4	7			1		13
18		1984			3				1	4
19		1985								
20		1986								1
21		1987								



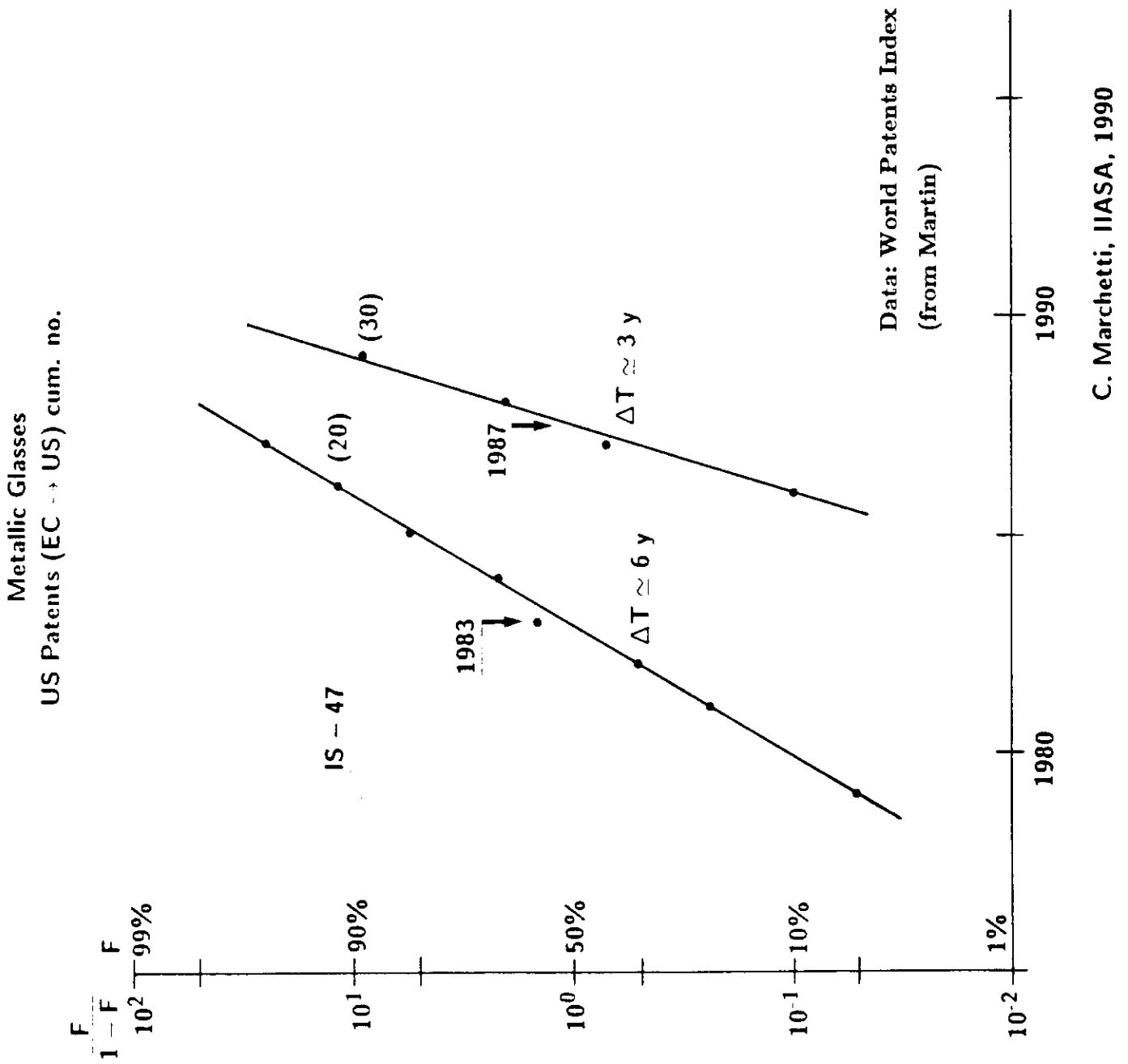
Figure 13.

METALLIC GLASSES  
US PATENT APPLICATIONS (EC → US)



C. Marchetti, IIASA, 1990

Figure 14.



C. Marchetti, IIASA, 1990

## Figures 13, 14.

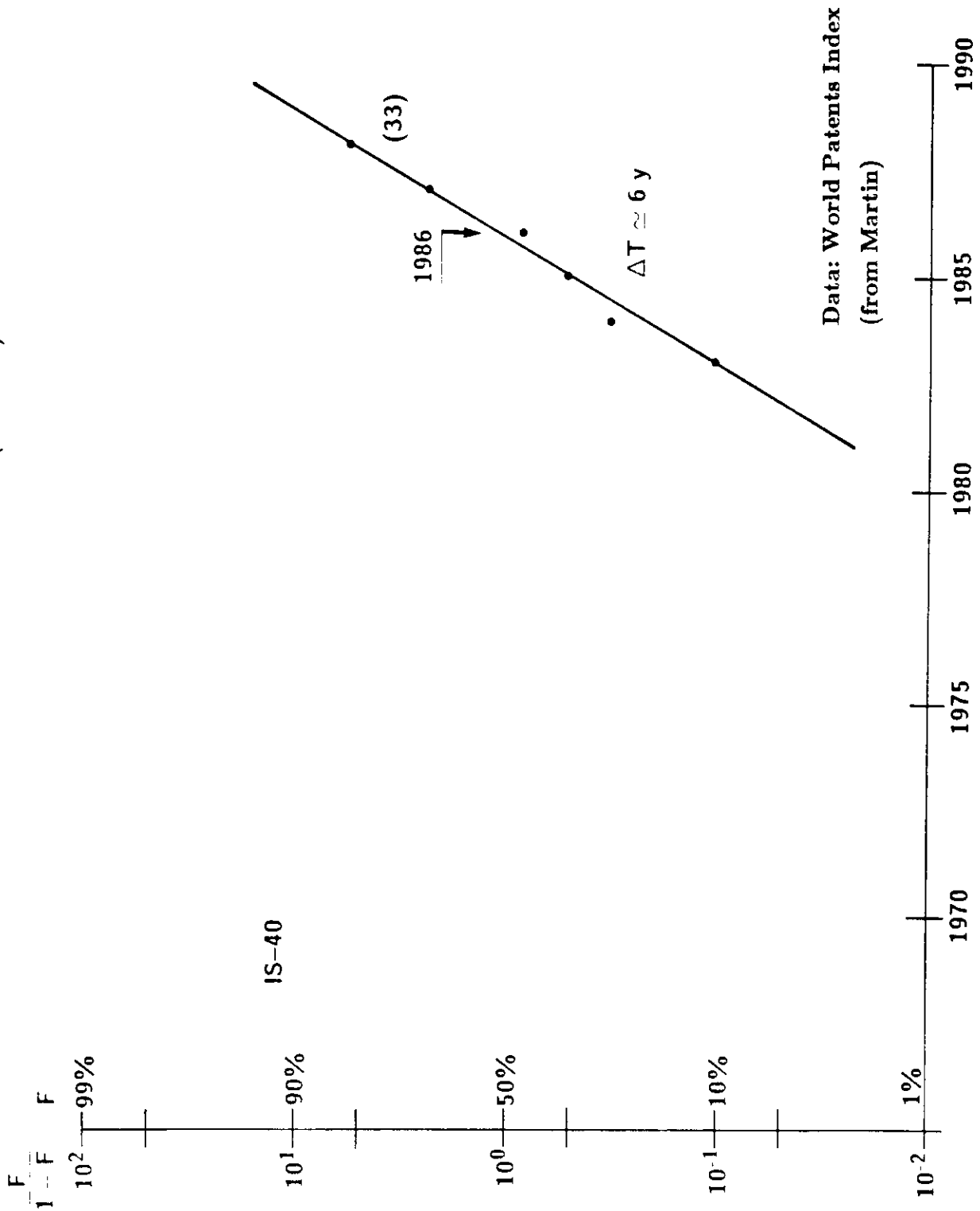
Coming from a nation (USA) to an area (EC) we have represented *EC patent applications for Metallic glasses in the USA* (Fig.13). There is apparently a single wave centered in 1986, although a number of applications escaped the count.

Patent granting is reported in Fig.14. It splits into two waves of 20 and 30 patents, respectively, centered in 1983 and in 1987. Most of these patents belong to Germany as we will see in the next charts. One point on which the interpretation skills should concentrate is that overall, both in applications and granting, it seems that *saturation for the last pulse is in sight*.

Obviously the start of a new pulse is always possible but one should be sure to have a brand new idea before launching into R&D in this area. The bandwagon era seems to be gone (or not begun yet).

Figure 15.

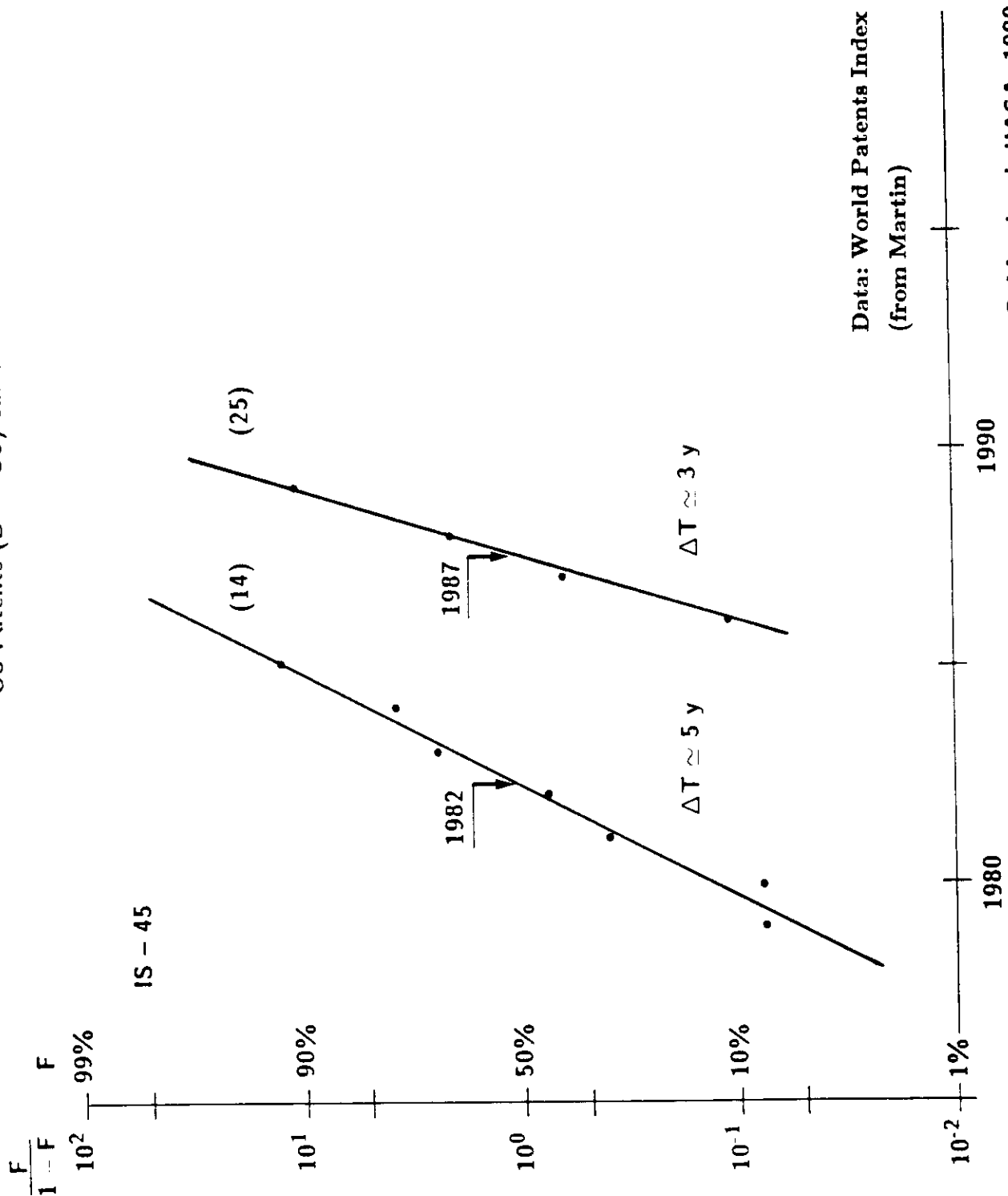
METALLIC GLASSES  
US PATENT APPLICATIONS (D → US)



C. Marchetti, IIASA, 1990

Figure 16.

Metallic Glasses  
 US Patents (D → US) cum. no.



Data: World Patents Index  
 (from Martin)

C. Marchetti, IIASA, 1990

## Figures 15, 16.

As inspection of the data has already shown, Germany is the most important generator of MG patents inside the EC. So I have decided to look at it in detail separating the data from those of the EC. The patents applied for in the USA are reported and analyzed in Fig.15. the wave is fairly late, being centered in 1986, but covers almost 80% of the applications from the EC.

The granting of the patents has two waves, centered in 1982 and in 1987. Some of the patents of the first wave do not appear in the counts of Fig.15, and this explains a certain (small) discrepancy between the two figures, including the sum of the saturation points giving 39 when the saturation point for the applications is only 33.

So Germany appears dominant in the EC, but it is dwarfed by the USA and by Japan, as we will see, which got  $\approx 320$  and  $\approx 150$  patents, respectively.

Figure 17.

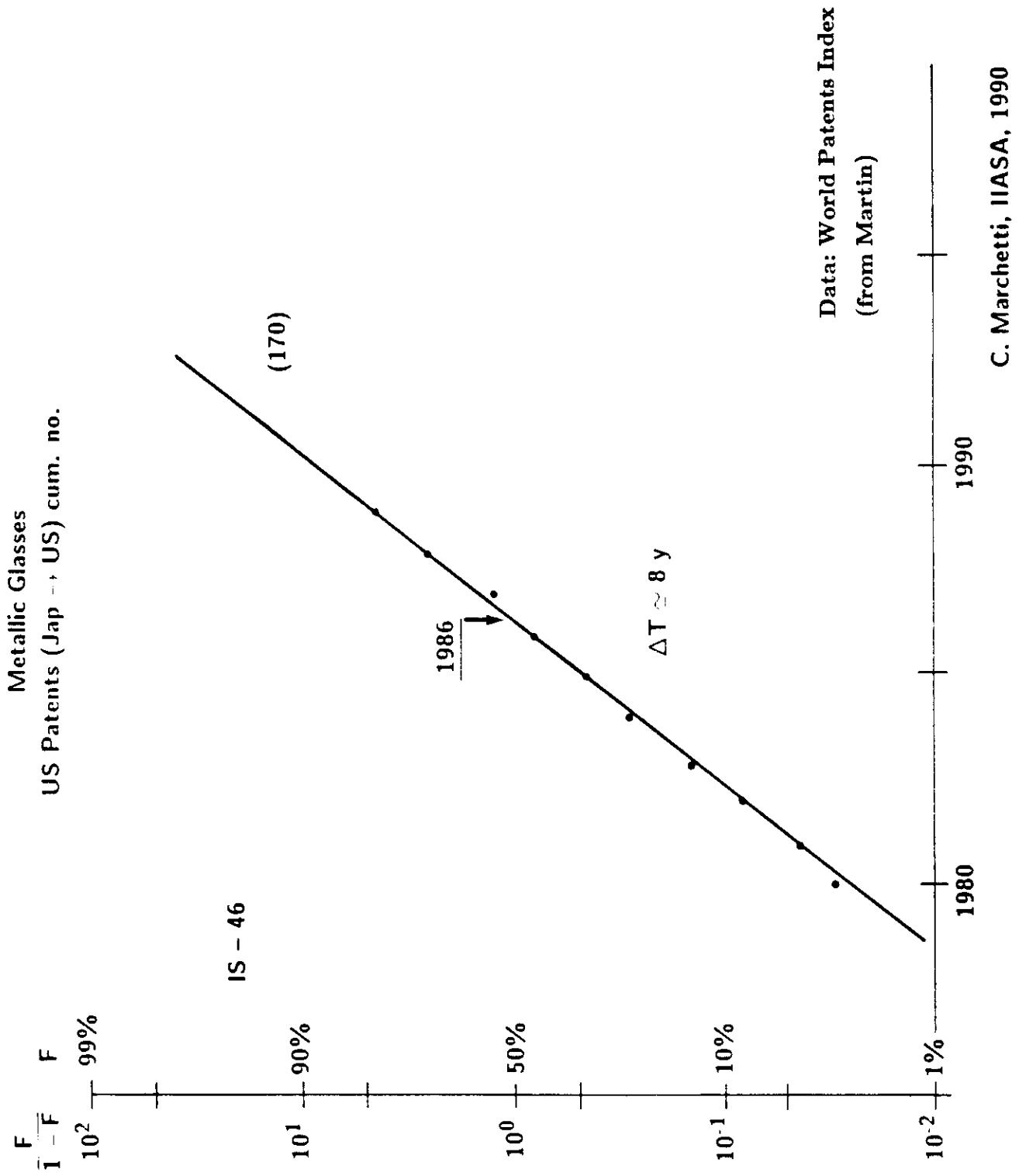
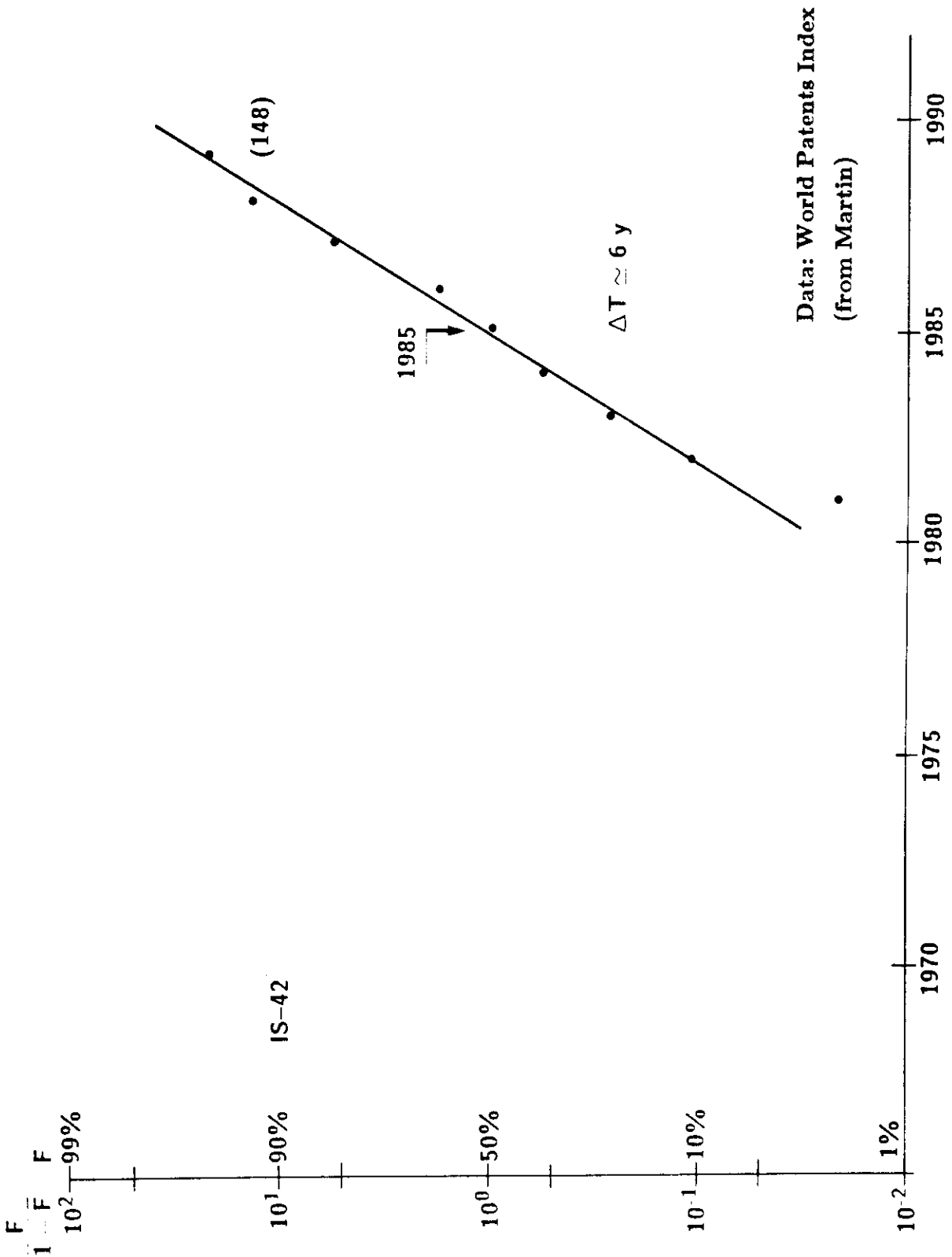


Figure 18.

METALLIC GLASSES  
US PATENT APPLICATIONS (J → US)



C. Marchetti, IIASA, 1990



## Figures 17, 18.

Japan is the great challenger of Western nations, and its R&D activity concentrates on subjects that may lead to a widespread technological dominance. Japan is very active in its research on advanced materials, especially ceramics where many new things reached already the shop floor. Also in this area that can open the view to revolutionary new machines with very large markets, like extra-low-loss electric transformers and motors, Japan has a leading edge on the rest of the world.

In June 1981, Hitachi Ltd. and its affiliate, Hitachi Metals, Ltd., succeeded in developing a method of mass-producing thin amorphous metal ribbon, about 10 cm wide and only 20 to 55 microns thick, on a continuous basis up to 300 meters in a single batch. At the same time, Sony announced its success in continuously producing a slender line of amorphous metal about 1 mm wide and 40 microns thick. The two developments opened new possibilities for applying such metals in the production of electric and electronic appliances, including television receivers and videotape-recorders.

## Rare Earths Cobalt Magnets

Magnetic alloys of many different types have been known since the early years of this century. However, great strides have been made in the past 20 years in terms of enhanced magnetic properties. To illustrate how much progress has been made in the development of magnetic materials, one need only look at the ratio of magnetic energy density to unit volume of material. This rose from about 1:1 to 12:1 from 1900 to 1967, but more than tripled in the last 20 years to its current level of about 40:1.

Significant advancements in magnetic materials began with the development of cobalt steels by the Japanese researchers Honda and Takagi in 1917. They found that these steels had a coercive force up to five times that of ordinary steel. The next significant advancement was by another Japanese, Mishima, in 1932. He discovered that certain nickel-aluminium-iron alloys had greater coercive forces than those of carbon steels. It was soon found that the addition of cobalt greatly increased coercive force further and made the alloy easier to treat for enhancing mechanical properties. This led to the aluminium-nickel-cobalt (Alnico) magnets still widely used today. However, one major deficiency of these magnets is their poor mechanical properties, which can restrict their use. The later development of ceramic barium and strontium ferrite magnets in the 1950s proved to be stiff competition for the Alnico type.

The discovery of the rare-earth cobalt magnet was a technological breakthrough in the field of magnetic materials, resulting in a sixfold increase in energy product. The  $\text{SmCo}_5$  magnet was first synthesized and characterized by K. Nassau, L.V. Cherry, and W.E. Wallace in 1960, and the first patent involving  $\text{SmCo}_5$  was issued to this team of researchers in 1963. Karl Strnat and colleagues at the University of Dayton were instrumental in its development. By measure of energy product and coercive force, these magnets proved greatly superior to Alnico magnets. Samarium, although relatively expensive, was the rare-earth element that achieved the best combination of properties for most applications and was cost-effective relative to other rare earths. The magnetic properties were so attractive that production of SmCo magnets had grown into a 100-million-per-year business in 1984.

SmCo magnets rapidly found uses where space is a premium and cost is not a limiting factor, particularly lightweight, electronic equipment. Earliest uses in electronic watches stepper motors, and replacing Alnicos in electron beam focusing systems, medical devices. New uses in servomotors, actuators, audiovisual products, headphones, loudspeakers, wiggler magnets in synchrotrons.

Figure 19.

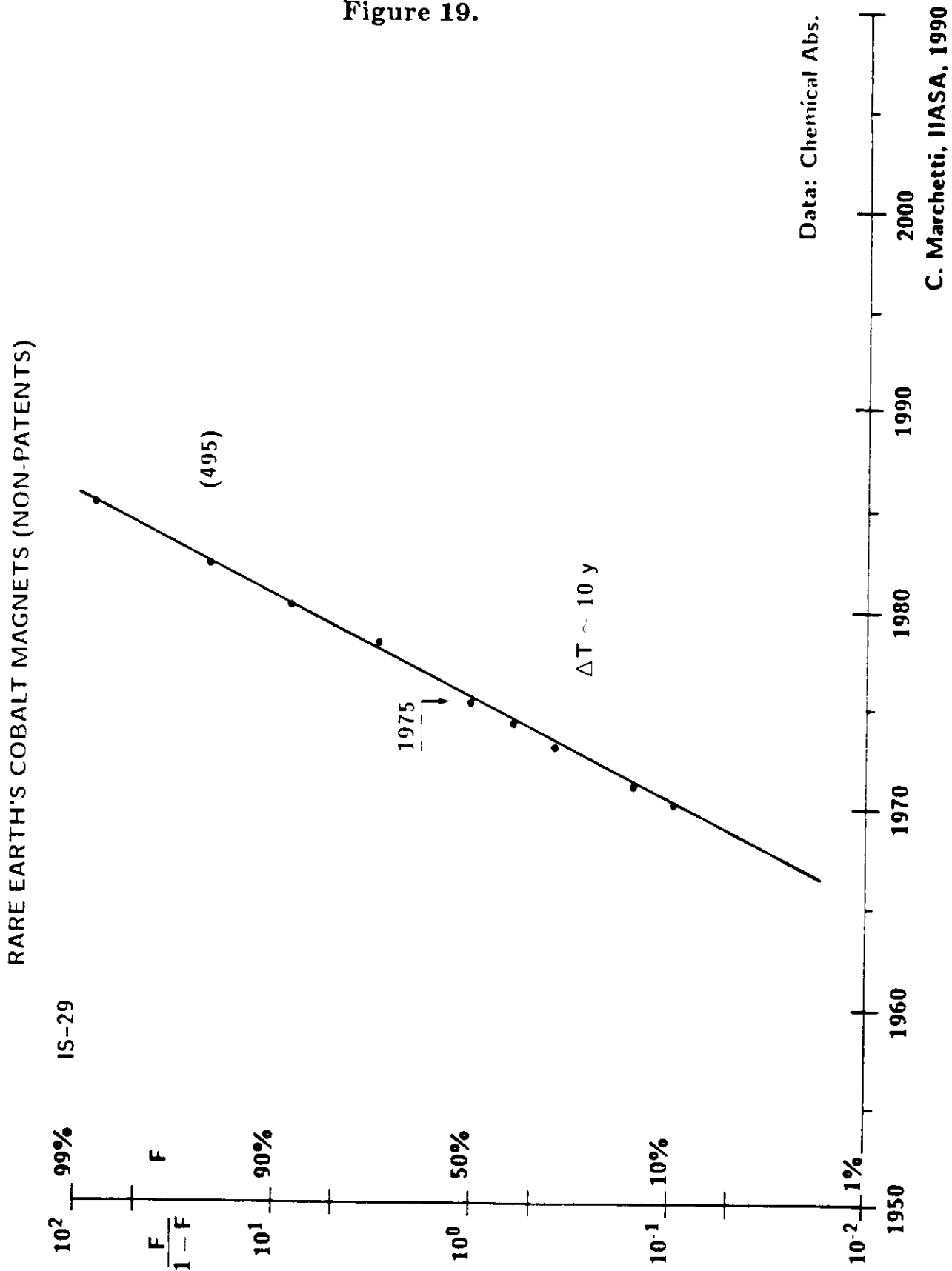
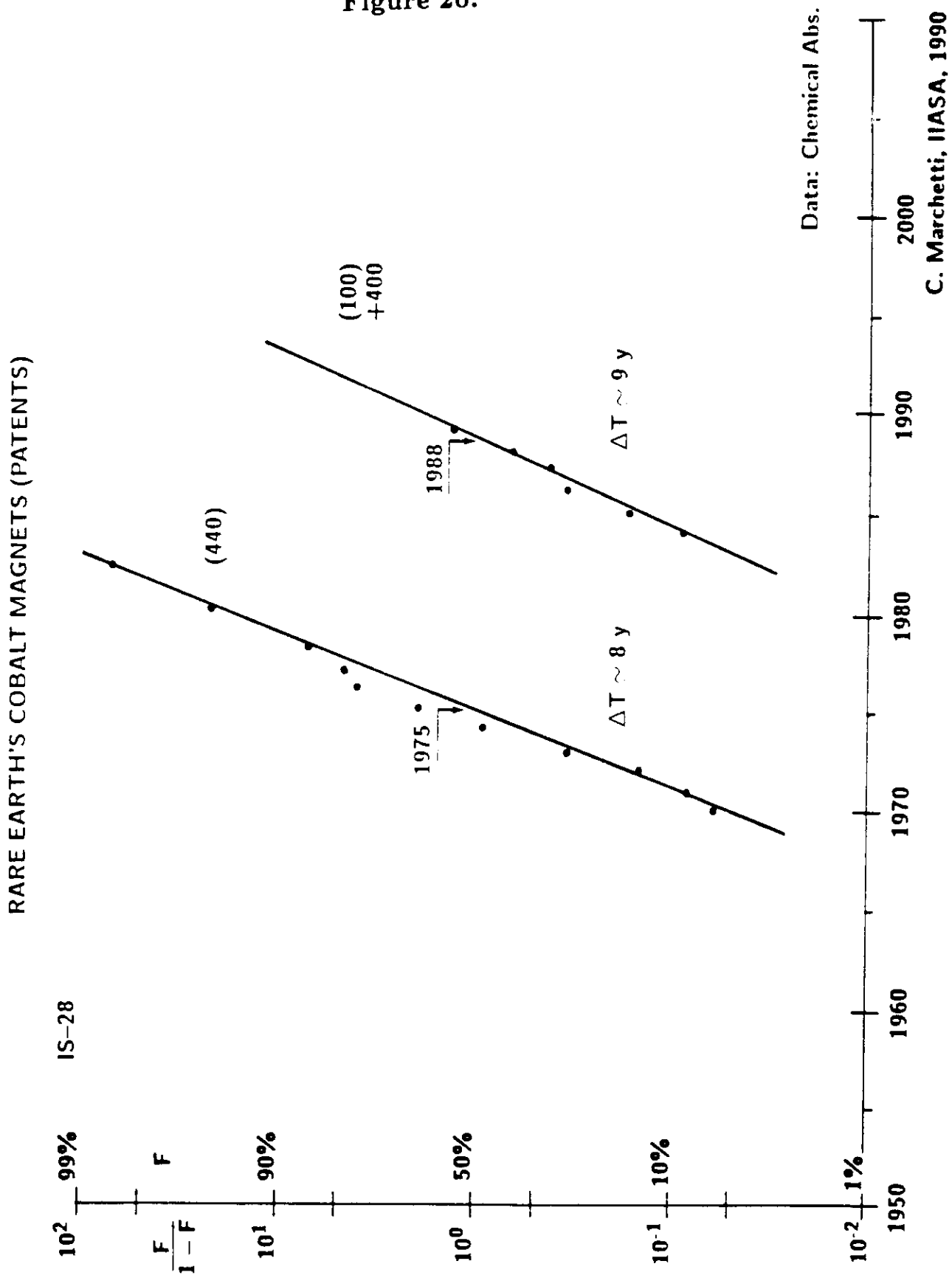


Figure 20.



## Figures 19, 20.

The case of *Rare Earth Cobalt Magnets* is analyzed here. Publications, saturating to 495 papers, are centered in 1975 with a time constant of 10 years (Fig.19). *Patents* on the contrary seem to organize in *two pulses*, one of 440 objects, more or less synchronous with publications, and a second one of 100 objects coming 13 years later with a similar time constant (Fig.20).

From the R&D strategic point of view, basic research seems to have come to a standstill. This means to restart it one should introduce some new ideas. From the point of view of patents there seem to be some space left during the next five years or so.

## Sialons

Si-Al-O-N compounds are made from the most abundant elements and this promises low prices together with a set of very interesting properties.

The general properties of Sialon ceramics can be summarized as:

- (1) High mechanical strength at ambient and elevated temperatures.
- (2) High specific strength resulting in weight savings over metallic systems.
- (3) High hardness, high toughness, and low coefficient of friction. This combination results in excellent wear, abrasion, and erosion resistance.
- (4) Low coefficient of thermal expansion leading to good thermal shock resistant.

Sialon ceramics are begin evaluated in a number of areas where materials have to operate at high stresses and elevated temperatures. Listed below are examples of current applications.

- (1) Engine components (diesel and petrol). Japanese companies are already marketing precombustion chambers and glow-plugs for diesel engines manufactured in Sialon ceramics. Field trials on diesel engine tappets were run to 70,000 km with negligible wear. British and European engine manufacturers are currently testing components made from Sialon and continue to show great interest in them.

- (2) Gas turbine engines. High-temperature Sialon ceramics have mechanical properties which, coupled with the possibility of turning them into complex shapes, make them ideally suited to this application. The primary advantage is the marked fuel efficiency gain in turbines. Potential applications include aerospace, land-based, and automotive turbines. Commercial automotive turbine engines are not expected for another decade – Sialon ceramics are being evaluated in long-term research programs toward this goal and have performed successfully in bearing trials.
- (3) Metal cutting. Indexable lathe inserts made out of the more glassy Sialon ceramic outperform cobalt-bonded tungsten carbide and alumina in cutting steel and superalloys.
- (4) Welding. This application covers both gas shrouds and location devices for resistance welding machines. Small diameter gas shrouds with a wall thickness of less than 1 mm are used in automatic welding operations in the aerospace industry. Sialon ceramic shrouds perform many thousands of cycles where normal alumina shrouds cannot withstand the thermal shock.
- (5) Wear part and extrusion dies. The ability of Sialon ceramic to operate in contact with metallic components with or without lubrication, and its ability to withstand high temperature and thermal shock, enables it to cope with a wide range of wear environments throughout manufacturing industry. Drawing dies, tube-drawing mandrel plugs and roll guide plates are all areas where major increases in life and productivity over tungsten carbide have been experienced.



Japanese industry and government are pouring money into the development of advanced ceramics, notably ceramic/carbon fiber composites that will be strong and light enough to make the outer skin of space planes and hypersonic aircraft. Hundreds of Japanese companies are pushing their development, with activity particularly concentrated in the Nagoya area, the traditional center of Japan's pottery industry and the home ground of Toyota. The first super-plastic crystal composite has been produced by a Japanese scientist, Fumikio Wakai, of Miti Laboratories in Nagoya.

Figure 21.

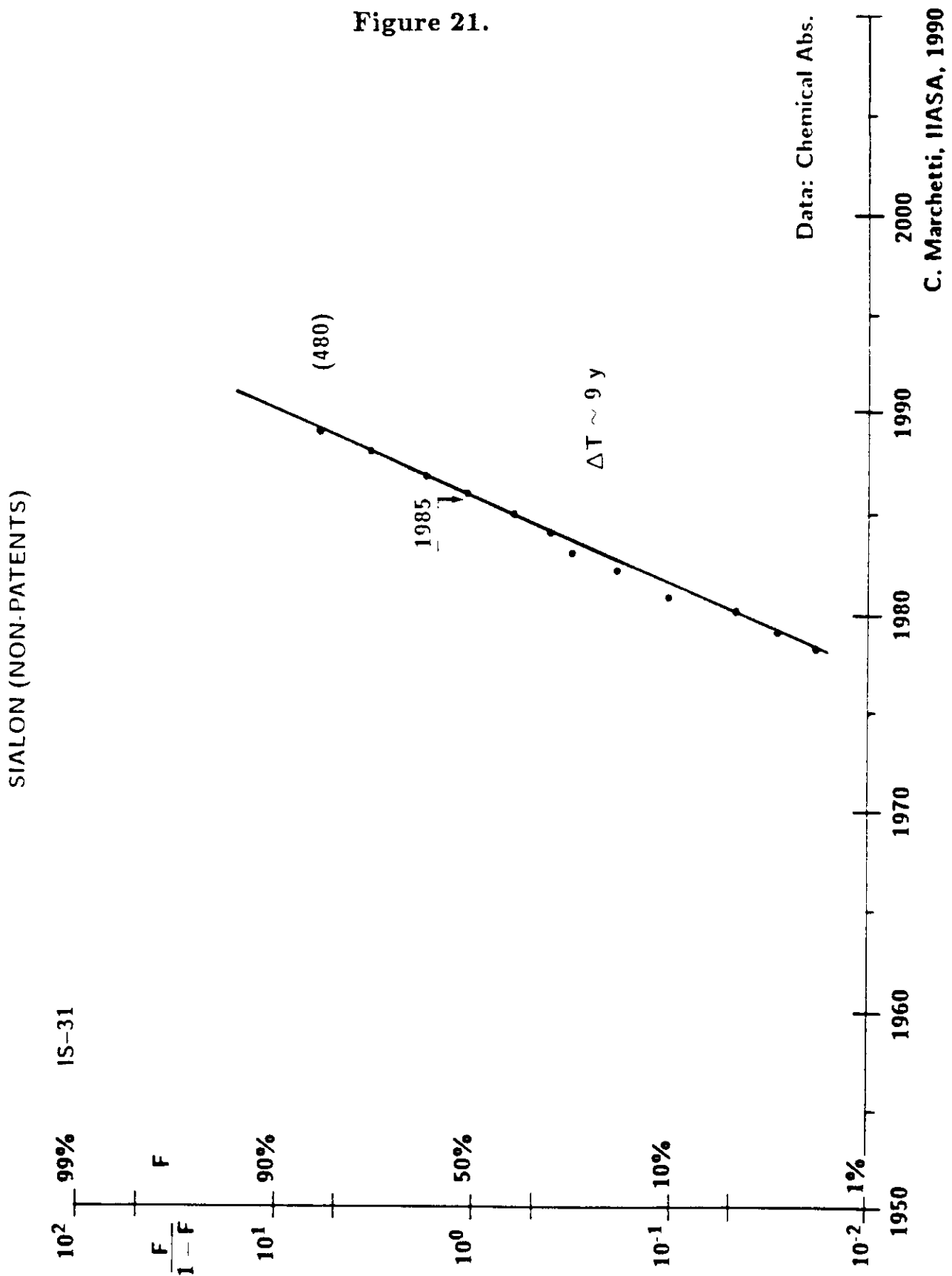


Figure 22.

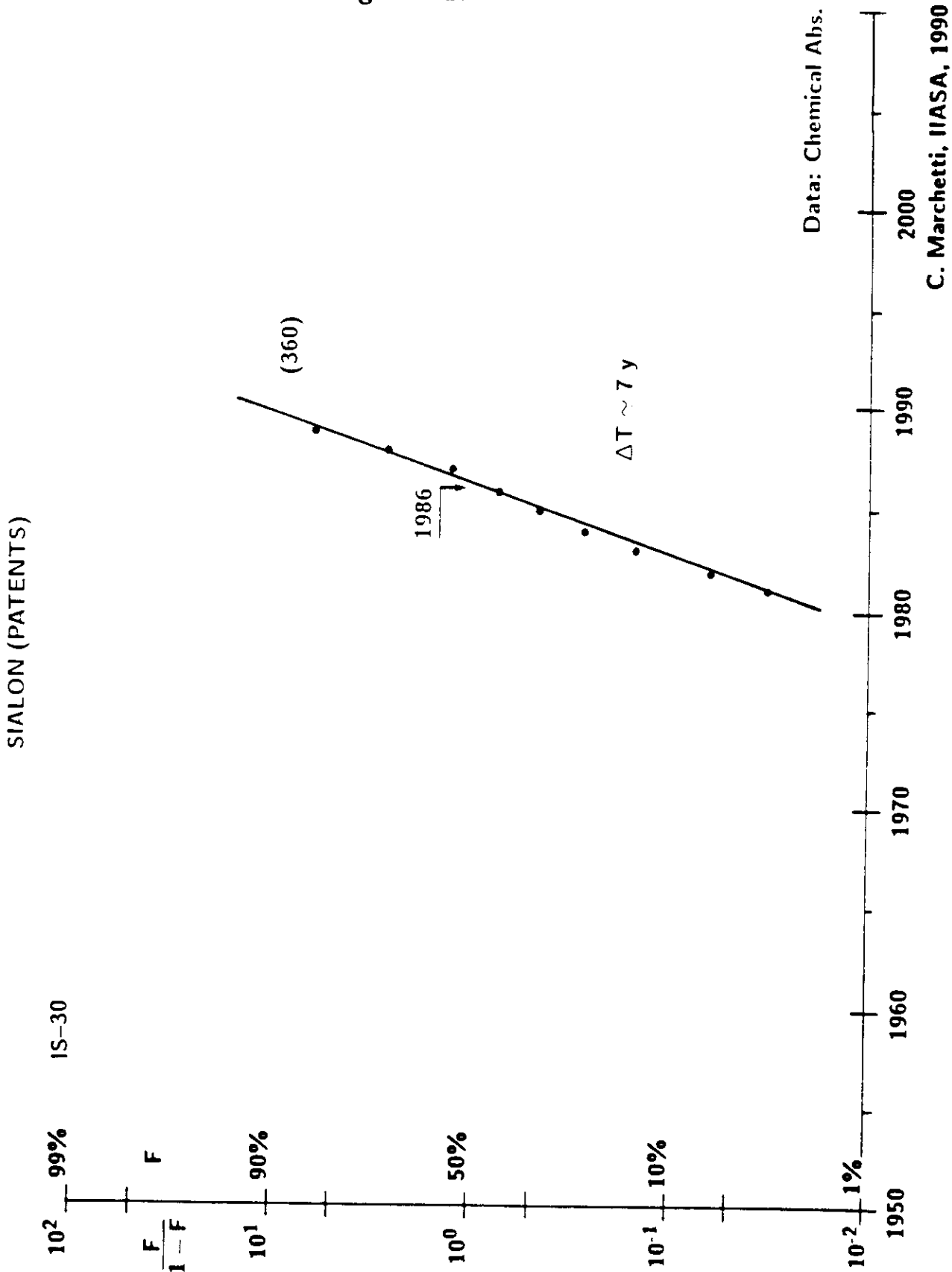
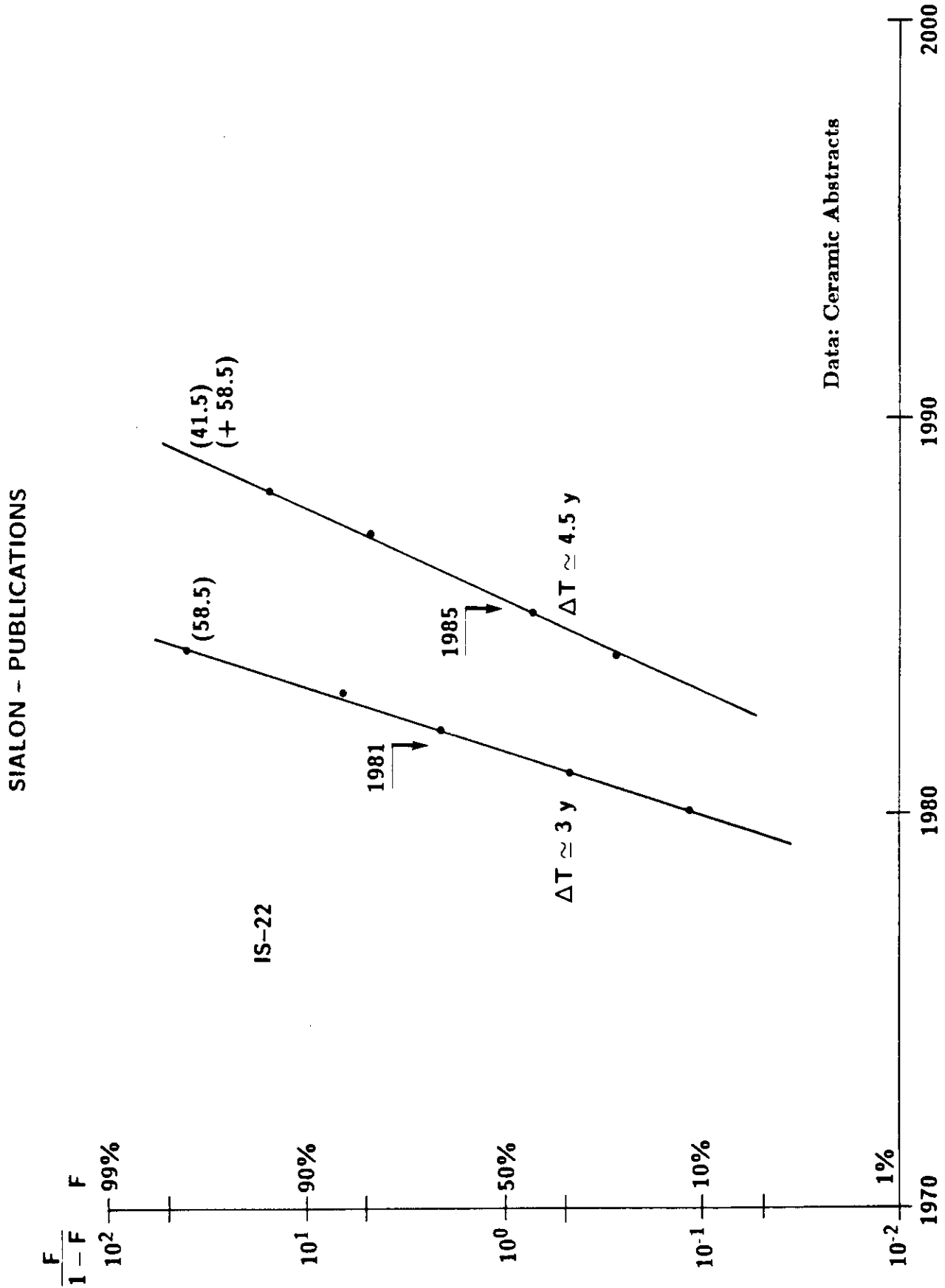


Figure 23.



C. Marchetti, IIASA, 1990

## Figures 21, 22, 23.

Taking *Chemical Abstracts* as a source of data, we look here at the case of *SIALON*, a group of ceramics of value for their hardness, toughness, mechanical strength, and specific strength. Fig.21 reports the analysis of publications with saturation point of 480 and centerpoint in 1985. Patents (granted) are analyzed in Fig.22. Saturation point is 360 patents and the centerpoint is in 1986. Time constants are respectively 9 years and 7 years. We are here clearly on a case where research and patenting seem to go together. *For precise statements on causes and effects one should peruse the whole set of papers and patents*, or representative samples. It is clear that the present waves of patents and publications are almost exhausted. They will be 90% respectively in 1993 and in 1994.

For the sake of comparison, we have also analyzed the publication lists of *Ceramic Abstracts* (Fig.23), which may be considered a more appropriate source of information if one is interested in the mechanical properties of these materials. The analysis shows a wave of publications exactly in tune with that of *Chemical Abstracts*, but preceded by another wave four years before.

## Thermotropic Liquid Crystals

### *Liquid Crystal Polymers*

Liquid crystal polymers (LCP) are a unique class of polymeric materials that exhibit a *highly ordered structure in the melt, solution, and solid states*. The morphology is tightly packed and highly ordered. LCPs have very high unidirectional mechanical properties as the molecules tend to be oriented in one direction. Wholly *aromatic copolyesters* in solid form have fiber-like areas uniformly dispersed throughout the material, giving it a wood-like structure described as self-reinforcing. They are classified as *thermotropic* and can be processed from a melt and injection molded into intricate shapes. *Aromatic polyamides* are classified as lyotropic and are solution-formed into fibers and films.

These high-performance thermoplastic resins exhibit strength 15 times that of steel and stiffness up to five times that of steel, aluminium, or glass fiber. In addition, they retain these properties at elevated temperatures. They are flame retardant, are resistant to chemicals, and creep is negligible.

### *Aromatic Copolyester*

Thermotropic LCPs exhibit outstanding chemical resistance, high dimensional stability, and are easily processible. Examples of the melt-processible LCPs available are Xydar (Amoco) and Vectra (Celanese Speciality Operations). Xydar resins were the first of this type to be introduced in late 1984 by Dartco Manufacturing Co.; the Xydar LCP business was sold to Amoco in 1988. Xydar LCP resins are based on terephthalic acid, p,p'-dihydroxybiphenyl, and p-hydroxybenzoic acid. The biphenol-base resins are available in unfilled and filled grades. Vectra resins are based on p-hydroxynaphthoic acid monomers. Over 70 variants of naphthalene-base resins have been developed, including extrusion grades and grades containing fillers.

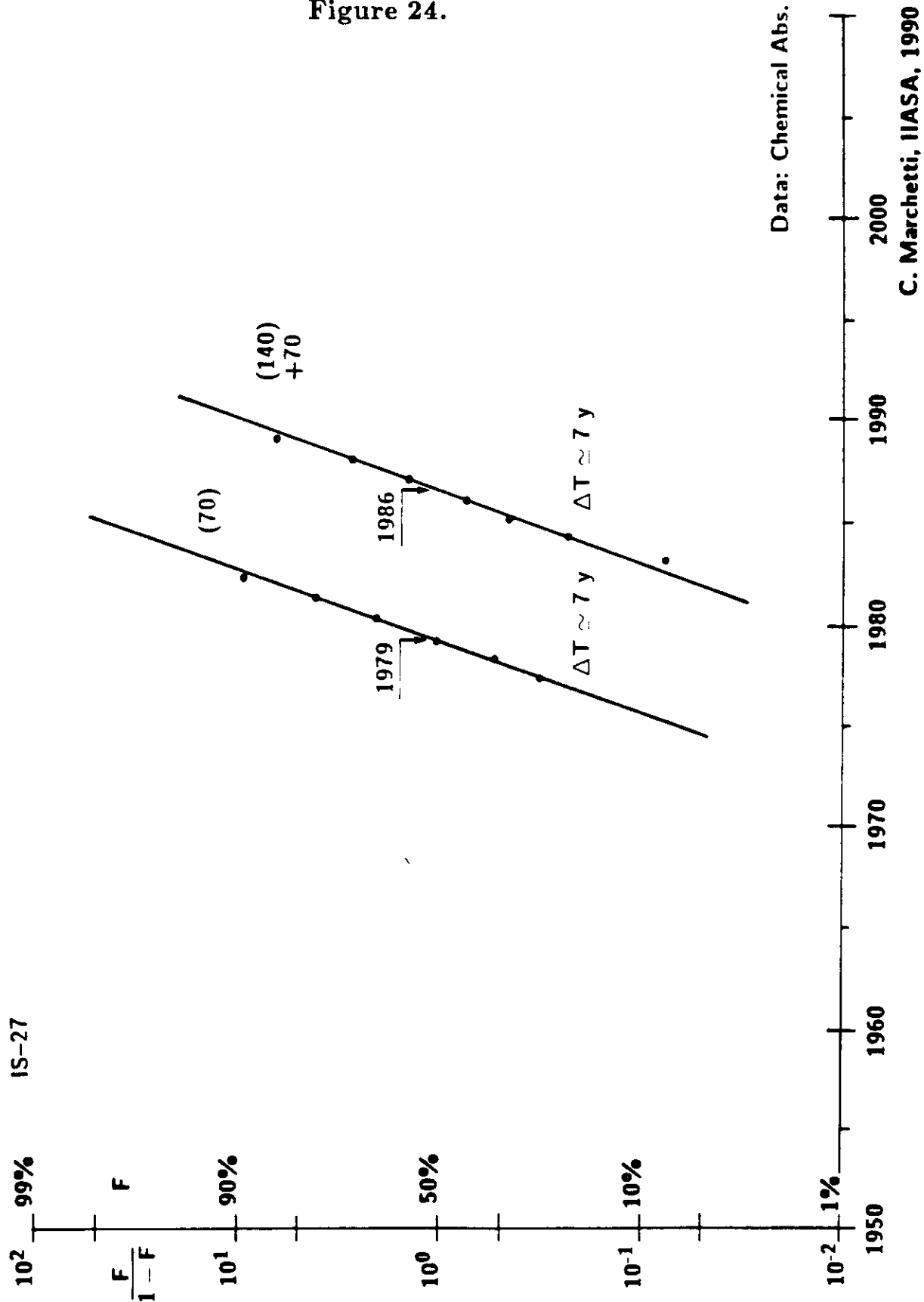
The LCP (aromatic copolyesters) have a high melting point, with biphenol-base resins having the higher of the two. Typical molding cycle times for naphthalene-base LCPs are between 10 and 20 seconds, versus 20 to 30 seconds for biphenol-base resins. The melt-processible LCPs can be molded into thin-walled parts at high speeds, and the high melt viscosity allows them to be molded into heavy-walled parts as well. The inherent lubricity and nonstick properties of these LCPs eliminate the need for a mold release. LCP resins have superior thermal stability, are extremely inert and resistant to virtually all chemicals, inherently flame retardant, can withstand high levels of UV radiation, and are transparent to microwaves. Applications include valve seats, electrical connectors, connectors, chemical pumps, and automotive and high-performance aircraft parts. Xydar is primarily consumed by Tupperware.

### *Aromatic Polyamide*

Lyotropic liquid crystal polymers are available as films or spun fibers. Spun fibers of aromatic polyamide are known by their generic name, aramid fibers. Development occurred in the early 1960s and characteristics include a higher heat tolerance than other polyamides, high-tenacity and high-modulus, which makes them ideal for use in tire cord reinforcement or in ballistic vests. One such high-performance fiber was introduced by DuPont in 1973. Kevlar or poly(p-phenylene terephthalamide) has outstanding dimensional stability, showing essentially no creep or shrinkage at high temperatures. Special processing techniques have had to be developed for aramid fibers because of the high melting point of aromatic polyamides and their poor stability in conventional solvents. Kevlar is wet spun from solution in concentrated sulfuric acid.

Figure 24.

THERMOTROPIC LIQUID CRYSTALS (NON-PATENTS)





THERMOTROPIC LIQUID CRYSTALS (PATENTS)

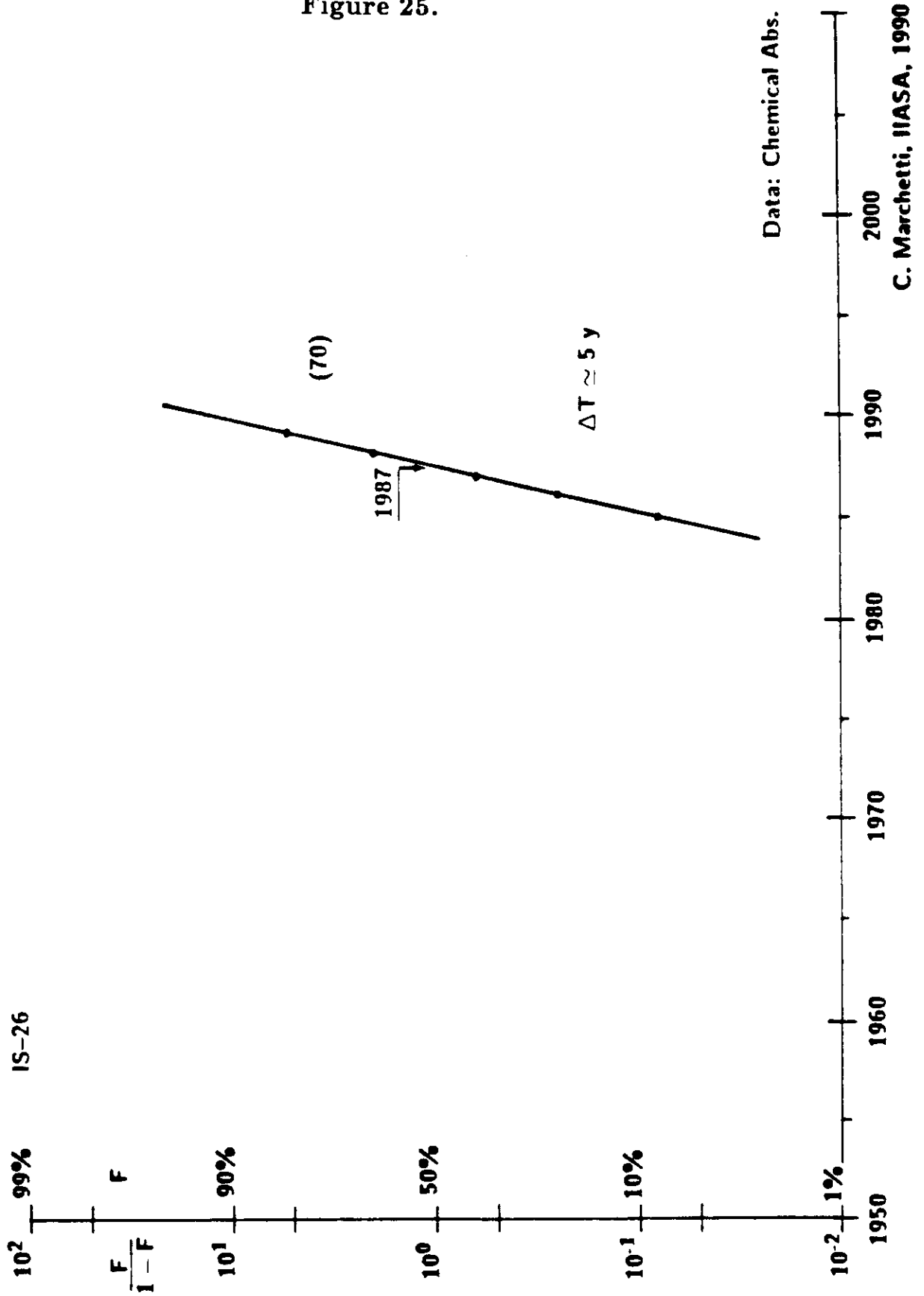


Figure 25.

## Figures 24, 25.

The case of *Thermotropic Liquid Crystals* presents still another kind of behavior. As shown in Fig.24 publications present two pulses centered in 1979 and 1986 with respectively 70 and 140 papers. The time constant is 7 years in both cases. Patents have a single pulse centered in 1987 with a time constant of 5 years (Fig.25). These patents are granted, so there is a couple of years distance from the application date. A publication may take one year to come out. The second pulse of publications and that of patents seems quite synchronous.