Title

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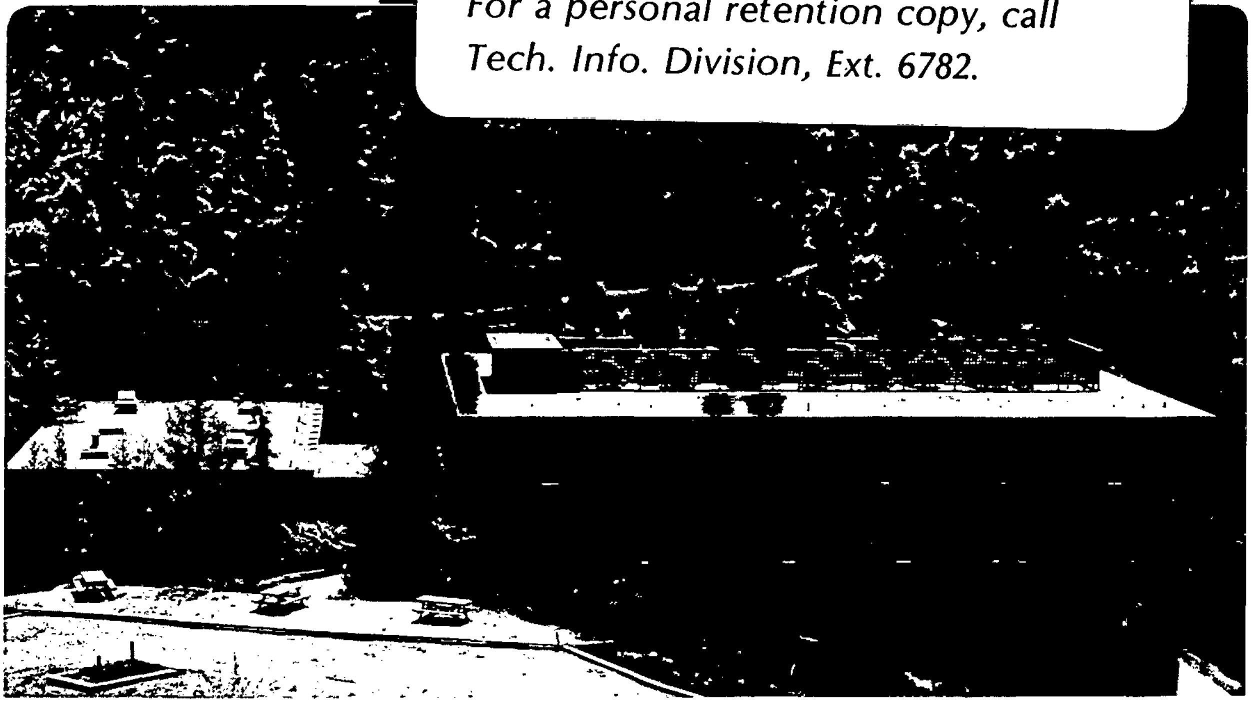

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PHOTODISSOCIATION OF WATER BY p- AND n-TYPE POLYCRYSTALLINE IRON OXIDES USING VISIBLE LIGHT (< 2.7 eV) IN THE ABSENCE OF EXTERNAL POTENTIAL

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ABSTRACT

A polycrystalline p/n diode assembly, consisting of pressed Mg- and Si-doped iron oxide powders, has been shown to photodissociate water using visible light in the absence of any external potential. In the investigated pH range (8-14) the device produces hydrogen catalytically in amounts which are readily detectable by gas chromatography. The relatively low power conversion efficient of 0.05% is believed to be due to the poor charge transfer properties of the p-type iron oxide used.

The photodissociation of water using strontium titanate single crystals or polycrystalline powders to produce hydrogen and oxygen has been studied intensively in recent years (1). When platinum was deposited over the oxide and alkali hydroxide was present at its surface illumination by band gap (3.1 eV) or larger photon energies produced hydrogen at rates of several molecules per site per second at 300K. When n-type $SrTiO_3$ or TiO_2 and p-type GaP or CdTe were used in an electrochemical cell as anode and cathode, respectively, the photodissociation of water could also be carried out without using external potential (2,3). The need of radiation in the ultraviolet, instead of the solar region however, seriously limits the utility of these systems for chemical conversion of solar energy. Recently it was shown that a p/n diode, consisting of single crystal p-GaP and polycrystalline n-Fe_2O_3, could split water at relatively low quantum yields when exposed to visible and near UV radiation (4).

We report the photodissociation of water by radiation in the solar region and in the absence of any external potential. This was accomplished by using samples that were made from silicon doped n-type and magnesium and silicon doped p-type iron oxide pressed polycrystalline disks. These were connected by a conducting silver epoxy as shown in Figure 1. The p- and n-type iron oxide disks were immersed in aqueous solutions of various pH where both disks were illuminated using radiation of $E \leqslant 2.7$ eV.

Hydrogen evolution was readily detectable with rates of several molecules per site per minute using visible light and without external potential. Photoinduced hydrogen production rates are given in Table I. The photoactivity slightly increases between pH = 8 and 12 while the number of detected hydrogen molecules is lowest at pH = 14. The pH dependence of the hydrogen evolution rate is under continued investigation.

A slow poisoning of the hydrogen production is observed as indicated from the data in Table I. Exposing the sample to air seems to regenerate its photoactivity and the same sample can be used in several experiments always giving the highest photoactivity during the first hour of exposure.

More than 3 x 10^{17} hydrogen molecules have been detected in single exposures so far. With an illuminated total p- and n-surface area of 0.6 cm^2 this amounts to hundreds of monolayers of hydrogen. Even if the real surface area of the pressed polycrystalline iron oxide pellets is larger, perhaps by one order of magnitude, the number of detected hydrogen molecules per surface site is of the order of 50. Thus, we believe that the photoinduced hydrogen evolution is catalytic.

Our apparatus, which permits the measurement of both the photocurrent and the hydrogen evolution simultaneously, is shown in Figure 2. It consists of an electrochemical glass cell and a closed circulation loop for transporting the photogenerated hydrogen, with Argon as a carrier gas and a circulation pump, to a gas chromatograph (Hewlett Packard 5720 A). The gas chromatograph, fitted with a thermal conductivity detector, has a detection limit for H_2 which corresponds to a production rate of 10^{16} molecules per hour in the cell. Air leaks in the cell and the circulation loop hinder accurate detection of the photoinduced oxygen production. The sample is illuminated by a 500 W lamp. The light passes through a water filter and a visible pass filter ($E \leq 2.7$ eV) to the sample.

n-Type iron oxide samples were prepared by mixing powders of α-Fe_2O_3 and SiO_2 to obtain compositions of $0 < Si/(Si + Fe) \leq 10$ atomic %, whereas p-type iron oxide samples were prepared by mixing powders of α-Fe_2O_3, MgO and SiO_2 so that $Mg/(Mg + Si + Fe)$ and $Si/(Mg + Si + Fe) = 10$ atomic %. The mixed powders were then pressed into pellets, heated in air at 1340-1390°C and rapidly cooled in air. The resulting resistivity of the samples was in the range of 10^3-10^5 Ω cm.

While the photocurrent is proportional to the hydrogen evolution rate for homogeneous materials this may not be the case for heterogeneous or polycrystalline materials such as our doped iron oxide polycrystalline pellets. The photoelectrons may recombine at grain boundaries and will not be detectable while the local photoreaction may still produce hydrogen. Electron microscope pictures of the n-type and p-type iron oxide samples (Figure 3) clearly show the structural heterogeneity. Scanning auger electron spectroscopy studies indicate the presence of a multiphase system that includes silicon enriched precipitates in addition to the silicon doped and magnesium doped iron oxide phases.

Blank experiments with no sample but with electrolyte and sample holder in the cell gave no detectable hydrogen production, either in the dark or under illumination. Furthermore, no hydrogen was detected in the dark when exposing the p- and n-type iron oxide surface to the electrolyte. Both iron oxide surfaces must be illuminated to obtain hydrogen evolution. The photocurrent obtained from the p-type iron oxide under potentiostatic conditions is considerably less (50 μA at 300 mV (RHE)) than that obtained from the n-type sample (500 μA at 1200 mV(RHE)). The relatively low hydrogen evolution rate may be due to the poorer charge transfer properties of the p-type iron oxide.

The efficiency of the device for photochemical energy conversion is poor, 0.05%. This is based on a production rate of 8×10^{16} hydrogen molecules per hour and incoming radiation with 17 mW power. However, improvement in the architecture of the cell, changes of the iron oxide stoichiometry and doping levels, and modification of the experimental conditions are likely to markedly improve the rate of hydrogen photoproduction in the near future.

The ability of polycrystalline iron oxide, doped only with Si or Mg, to catalyze the production of hydrogen upon solar irradiation raises the question of the possible importance of this system during the evolution of our planet.

The abundance of iron-magnesium-silicon compounds in the mantle assures that hydrogen and oxygen could be photoproduced from water with great probability and in large quantities. Once hydrogen is available its subsequent catalyzed reactions with CO_2 and N_2 to produce hydrocarbons and ammonia are thermodynamically feasible. Iron compounds are also excellent catalysts for these reactions and are used commercially in the chemical technology for this purpose. Thus, the series of reactions that begin with the photodissociation of water can yield organic molecules and oxygen and thus, result in photosynthesis. Photosynthesis by inorganic catalysts like the iron compounds in the mantle may have been of key importance for evolution in the pre-chlorophyl era of the planet.

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REFERENCES

1. Wagner, F.T. & Somorjai, G.A. (1980) J. Am. Chem. Soc. 102, 5494.
2. Nozik, A.J. (1976) Appl. Phys. Letters 29, 150.
3. Ohashi K., McCann, J. & Bockris, J.O'M. (1977) Nature 266, 610.
4. Mettee, H., Otvos, J.W. & Calvin M. (1981) Solar Energy Mat. 4, 443.

TABLE I: H_2 Production Rates [in units of 10^{16} H_2 molecules/hour]

n-type iron oxide: Si/Si + Fe = 1 atom %

p-type iron oxide: Si/Mg + Si + Fe = 10 atom %
Mg/Mg + Si + Fe = 10 atom %

Solution:	Dist. H_2O pH ≃ 8	0.01 N NaOH pH ≃ 12	3N NaOH pH ≃ 14
1st hour	6	8	2
2nd hour	3.5	6	5
3rd hour	2	5	---

FIGURE CAPTIONS

Figure 1: Platinized p-type and n-type iron oxide polycrystalline disks connected by conducting Ag epoxy.

Figure 2: Apparatus for simultaneous photocurrent and gas evolution studies.

Figure 3: Scanning Electron Microscope photographs showing n-type Fe2Si (left) and p-type Fe10Si10Mg (right). The samples consist of a Si- (left) and Si- and Mg- (right) doped Fe_2O_3 matrix and highly Si-enriched precipitates.

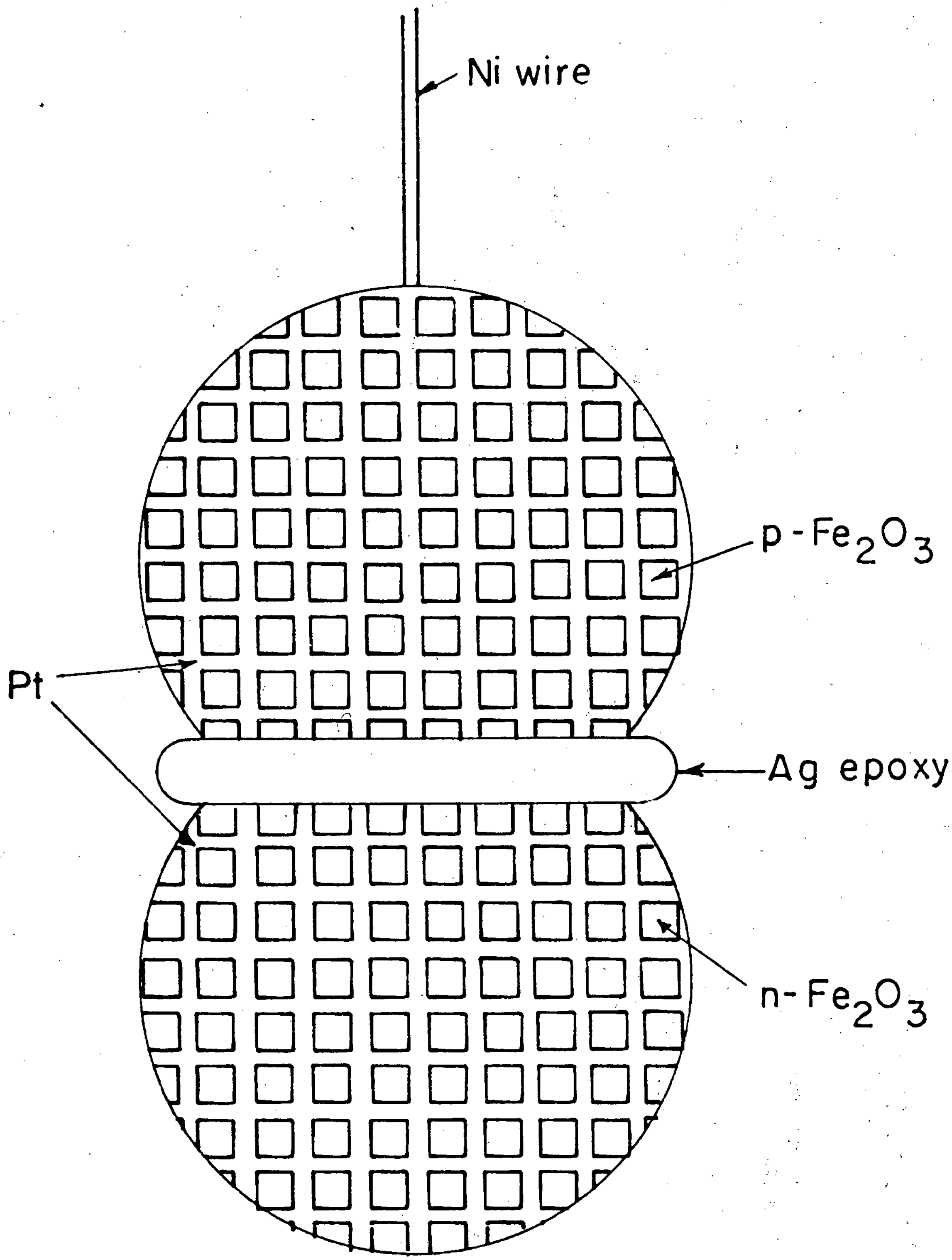

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Fig. 1

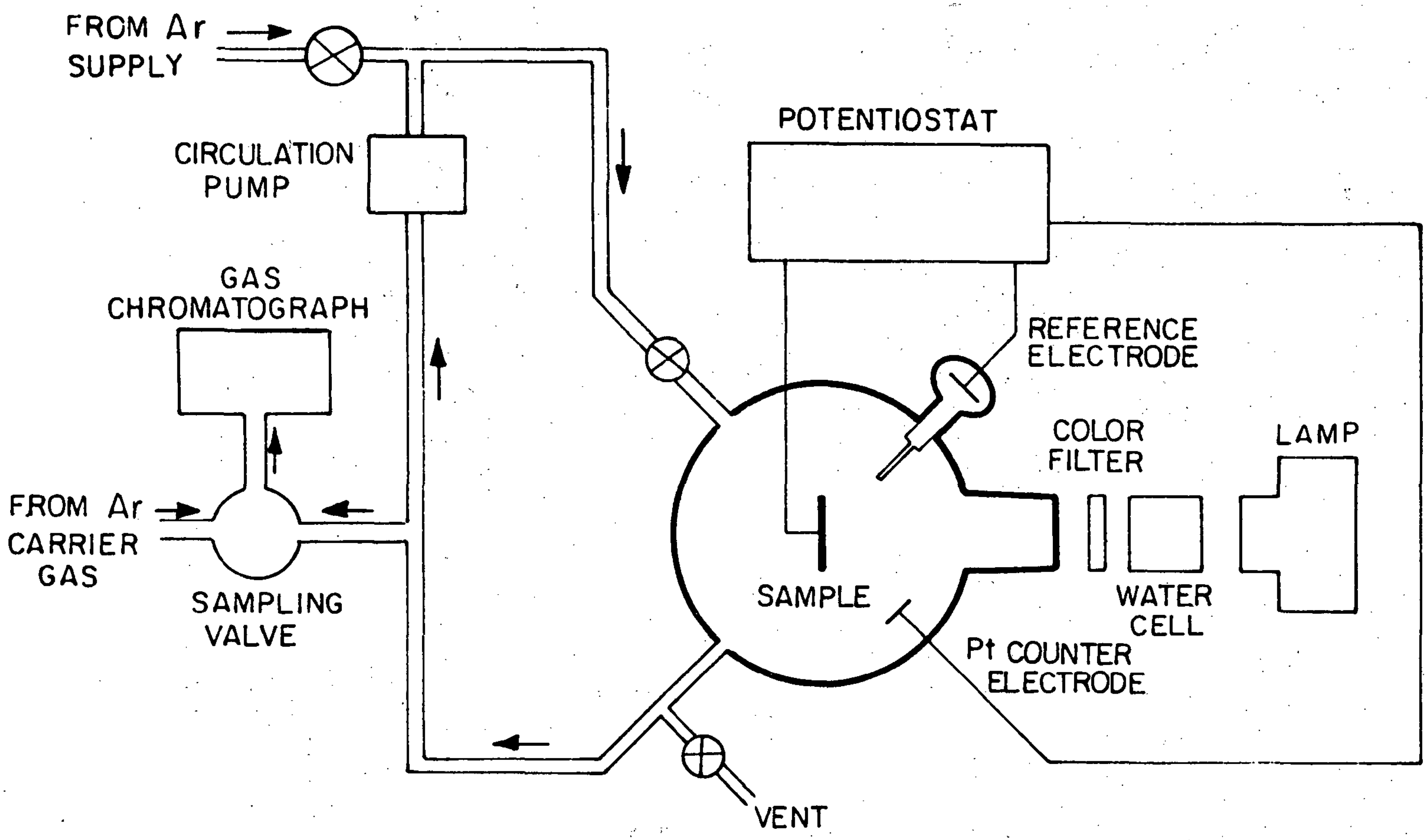

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Fig. 2

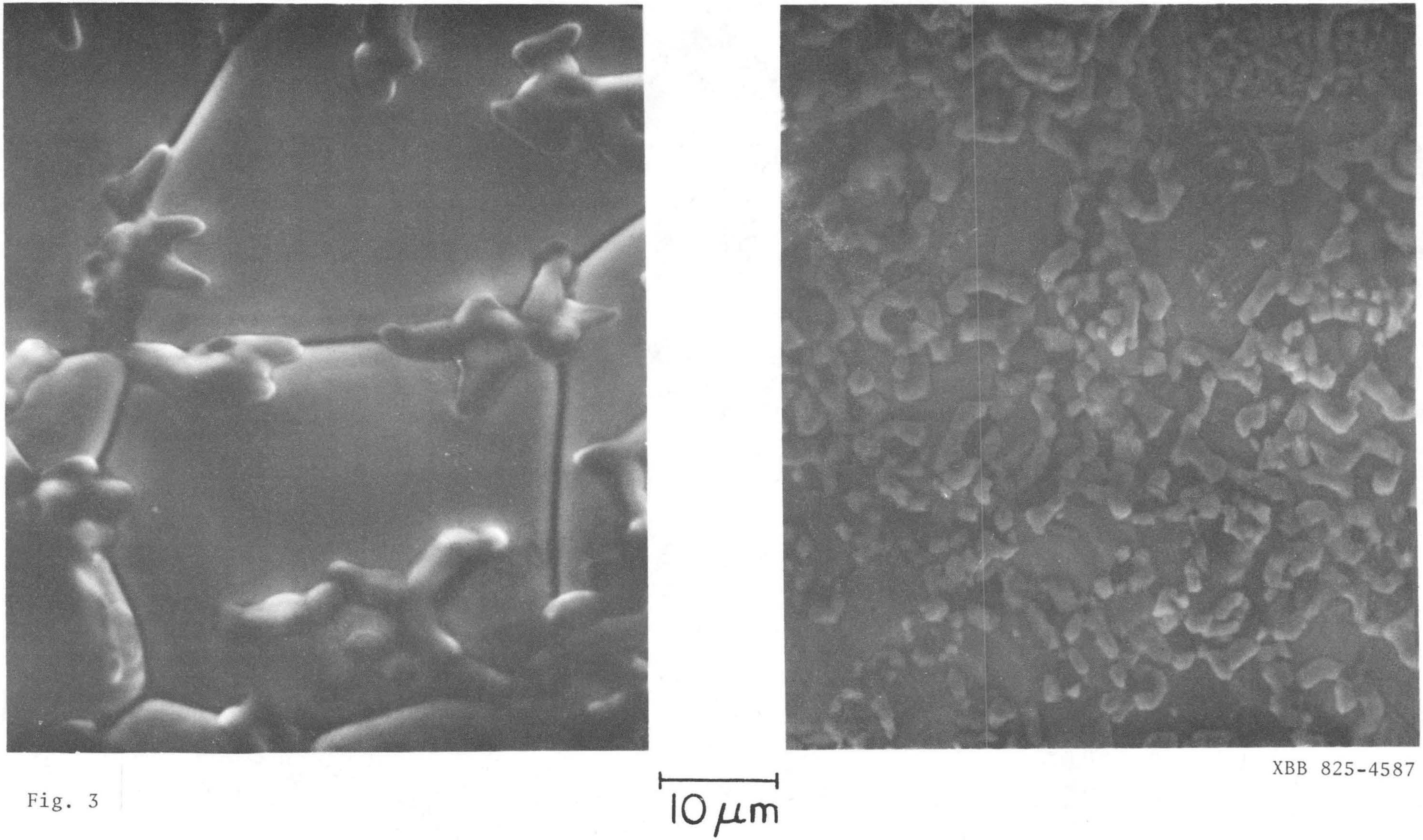

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Fig. 3

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