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FIELD ION METALLOGRAPHY

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1. Introduction

The field ion microscope [1,2] has a resolution of 2-3 Å and promises an understanding of all phenomena important in physical metallurgy in terms of the basic structural unit -- the atom. In the fifteen years that have elapsed since Professor Müller[3] developed this unique tool, exciting advances have occurred. Amongst these one may point to the first direct observation of vacancies and interstitials, [1] a theory for the atomic configuration at high angle boundaries, [4] the study of radiation damage in atomic detail[5] and an atomic view of surface diffusion.[6] This article discusses the place of the field ion microscope on the armoury of the metallographer in terms of its past achievements and future potential.

The field ion microscope is inherently a simple instrument (Fig. 1). The specimen is usually in the form of a thin wire and has a sharp tip at the end (radius of $\sim$ 100 Å). The microscope is evacuated to a pressure of 5×10^{-8} torr and the specimen is cooled with liquid nitrogen. Recently considerable work has been done using liquid neon, hydrogen and helium which achieve lower temperatures and lead to improved image quality. An image gas, usually helium, neon or hydrogen is admitted to the microscope at a pressure of a few microns.

A high positive potential is applied to the specimen. High field regions, F_c, exist over protruding atoms on the surface of the specimen. The helium gas is ionized over these regions and then the helium ions form an image on a fluorescent screen at a few centimeters from the specimen. The image is approximately a stereographic projection of the tip. At higher fields, F_e, the metal atoms themselves are ionized and the surface layer can be removed by this process, known as field evaporation. It is obvious that for successful field ion microscopy $F_e >> F_c$. For a given metal this condition can be achieved by either lowering the temperature or by changing over to an image gas of lower ionization potential. Thus there is no serious limitation on the metals that can be imaged. With the use of an image intensifier McLane and Müller[7] have succeeded in obtaining images from twenty-four metals. These include the refractory metals, like tungsten and iridium and the less refractory ones like copper, gold, and iron. As a technical feat of no mean order, they have also obtained images from aluminum and tin.

2. Applications

The field ion microscope had found diverse applications. In chemistry it has been used to study absorption and corrosion. Biophysicists are engaged upon the task of getting images from macromolecules. The microscope is firmly established as a valuable tool for metallography due mainly to the efforts of Professor Müller and his colleagues in Pennsylvania and D. G. Brandon and his coworkers at Cambridge. The following is a brief summary of their results on lattice imperfections, alloys and radiation damage. It is convenient to regroup them under crystallography, composition and topography. These three terms serve to characterize the

state of the metal and relate it to its mechanical properties - the aim of the metallographer.

2.1 Crystallography

Figure 2 shows the helium field ion micrograph of a tungsten specimen of about 300 Å radius of curvature. Each bright spot corresponds to a single atom on the specimen surface and the rings of atoms are the edges of planes in the crystal lattice. (110), (112), (100) and (111) planes appear prominently as is to be expected from a consideration of the atomic density of these planes. In the case of a fcc metal like iridium (111), (100), (113), and (110) planes predominate.

The distribution of lattice sites on the various crystal planes has been tackled on a purely geometrical basis by Nicholas.[8] As part of this programme Moore[9] has tried to account for the pattern in a field ion micrograph. His analysis is elegant. A sphere was imagined to cut an infinitely extended crystal and all the material outside the sphere removed. A computer was used to plot in orthographic projection the position of atoms that are within a certain distance from the surface of the sphere. The resulting pattern had a striking resemblance to the field ion image. The reverse process of feeding information from field ion images into computers holds exciting possibilities of making full use of the 10^4 bits of information inherent in each field ion micrograph.

It is of interest to note that the field ion images from tungsten, molybdenum, tantalum and iron appear different though they have the same type of arrangement of atoms. This mainly arises from the differing work functions of various planes. Besides, details of the electronic structure at the surface of metals are only beginning to be understood. Field ion

microscopes can play a useful part in elucidating these details.

The geometrical information in a field ion micrograph is easily evaluated. Indexing of the various planes can be done by using symmetry considerations. The number of rings can be counted and this can be used to find out tip radius, magnification, etc. Defects can also be analyzed. Field evaporation can be used for a three dimensional reconstruction of the lattice - a truly amazing feature of the everyday operation of the microscope.

2.2 Composition

Next to the configuration of atoms, their composition is of interest. Alloy studies have been somewhat disappointing, however. A question on which the final word is yet to be said is that of distinguishing between atomic species. The alloy surface tends to be atomically "rough" and consequently the micrograph exhibits a degree of randomness. Ralph and Brandon[10] found that it was possible to distinguish between alloy species by voltage analysis. If the number of spots is plotted against voltage for a given surface, the graph is linear for tungsten. In the case of tungsten 26% rhenium alloy, the graph exhibited a discontinuity and this corresponded to the amount of rhenium present. Recent work by Brenner[11] has shown that the method is subjective and that a more careful and possibly tedious analysis of the micrographs is necessary.

While random solid solutions give rise to irregular field ion micrographs, ordered alloys give highly perfect images. Indeed it is possible to devise a new parameter for order from field ion micrographs. The study of cobalt-platinum alloys by Ralph and Brandon[12] now ranks as a classic. The equiatomic alloy has the face centered cubic structure in the disordered state, on ordering alternate (002) planes are occupied by cobalt and

platinum atoms respectively and the structure becomes tetragonal. Figure 3 brings out the beautiful symmetry in this state.

2.3 Topography

The connection between the nearly hemispherical surface of a metal tip and its field ion image is essentially topological in character. Thus there is a one-to-one correspondence between the protruding atoms on the surface of the specimen and the bright spots on the image. Vacancies are seen as such in the micrographs. The nature of contrast to be expected from an interstitial atom is not well understood. Dislocations have proved more elusive to image than grain boundaries. The extent of the contributions of field ion microscopy to the direct observation of dislocations is only two pages in Amelinckx's recent classic on the subject. That these two pages constitute a chapter at the same time foreshadows the importance of the contribution that field ion microscopy promises.

A major contribution from field ion microscopy is the development of a theory from the atomic configuration at high angle boundaries by Brandon, Ralph, Ranganathan and Wald[13,14,15]. They established that high angle grain boundaries have narrow widths and often have ledges a few angstroms in height. This observation fits in with their theory which uses the concept of a coincidence site lattice. Rotational symmetry operations on a lattice bring it into complete self-coincidence. However, partial self-coincidence can occur for certain other rotations about an axis. Two crystal lattices related by such an angular rotation about an axis have certain common sites, located on a single lattice of larger cell dimensions, known as the coincidence site lattice. Boundaries between crystals so related can minimize their energy by following planes of dense coincidence. A grain boundary running at a small angle to this

plane will take up a stepped structure such that it has a maximum surface area in the closepacked planes of the coincidence site lattice, analogous to a dislocation constrained to lie along a direction that is not a low energy direction. The twin boundary in Fig. 4 shows the dislocation structure generated at such a ledge.[4] A boundary not possessing the special relationship described above can be considered to be composed of a coincidence site lattice boundary and an associated sub-boundary to account for the angular deviation.

Radiation damage can be used to introduce imperfections on a scale suitable for field ion microscopy. Such damage can be introduced in bulk specimens which can then be thinned and studied. Vacancies and vacancy clusters have been observed in several studies.[5] It is also possible to introduce damage in situ: e.g., by placing an α-source very close to the specimen. Such experiments have dramatically brought out the damage due to the passage of an α-particle through the specimen.[16] These experiments also provide evidence for channeling and focusing of the particles used for bombardment. A somewhat similar experiment where a high energy fission fragment passed through the specimen gave the result shown in Fig. 5. The crater is nearly hemispherical and has a radius of about 250 Å.

3. Discussion

Much valuable work remains to be done. Recently a number of new groups has entered the field. With the increased volume of work, one might expect new advances. While it must be conceded that the field ion microscope is not a versatile tool, there are problems to which it is uniquely suited. Some of these have already been discussed. Future work might essentially employ less refractory metals like iron and nickel and repeat and enlarge the observations already made. As just one example of

the prizes that await the patient experimenter, one might point to the imaging of the Guinier-Preston zones in a nickel-beryllium alloy by McLane and Müller. This was reported at the twelfth annual field emission symposium in Pennsylvania. (Incidentally this event celebrated on location the tenth anniversary of the development of the low temperature version of the field ion microscope). Their micrographs show the zones as a bright band and provide clear evidence for coherence in atomic detail.

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REFERENCES

1. E. W. Müller, Adv. Electron. Electron Phys., 13, 83 (1960).

2. D. G. Brandon, Brit. J. Appl. Phys., 14, 474 (1963).

3. E. W. Müller, Z. Physik, 131, 136 (1937).

4. S. Ranganathan, Ph.D. Thesis, Cambridge University (1965).

5. D. G. Brandon and M. Wald, Phil. Mag., 6, 1035 (1961).

6. G. Ehrlich, 12th Field Emission Symposium, State College, Pennsylvania, 1965.

7. B. McLane, Master's Thesis, University of Pennsylvania, 1965.

8. J. F. Nicholas, An Atlas of Crystal Structures, Gordon and Breach Science Publishers, New York, 1965.

9. A. J. W. Moore, J. Phys. Chem. Solids, 23, 907 (1962).

10. B. Ralph and D. G. Brandon, Phil. Mag., 8, 919 (1963).

11. S. S. Brenner, AIME Conference on High Temperature and High Resolution Microscopy, Chicago, 1965.

12. B. Ralph and D. G. Brandon, Journées Internationales des Applications du Cobalt, 9-11, June, p. 76, 1964.

13. D. G. Brandon, R. Ralph, S. Ranganathan and M. Wald, Acta Met., 12, 813 (1964).

14. S. Ranganathan and A. H. Cottrell, p. 163, "Electron Microscopy 1964", Prague, 1964.

15. J. A. Hren, Acta Met., 13, 479 (1965).

16. M. K. Sinna and E. W. Müller, J. Appl. Phys., 35, 1256 (1964).

FIGURE CAPTIONS

Fig. 1 A Schematic Diagram of a Field Ion Microscope Tube

Fig. 2 Helium Field Ion Micrograph from a Tungsten Specimen

Fig. 3 Equiatomic Cobalt-Platinum in the Ordered State (H. N. Southworth).

Fig. 4 Dislocation Structure at a Twin Boundary in Tungsten

Fig. 5 Surface Crater in a Tungsten Specimen Formed by a Uranium Fission Fragment (K. M. Bowkett)

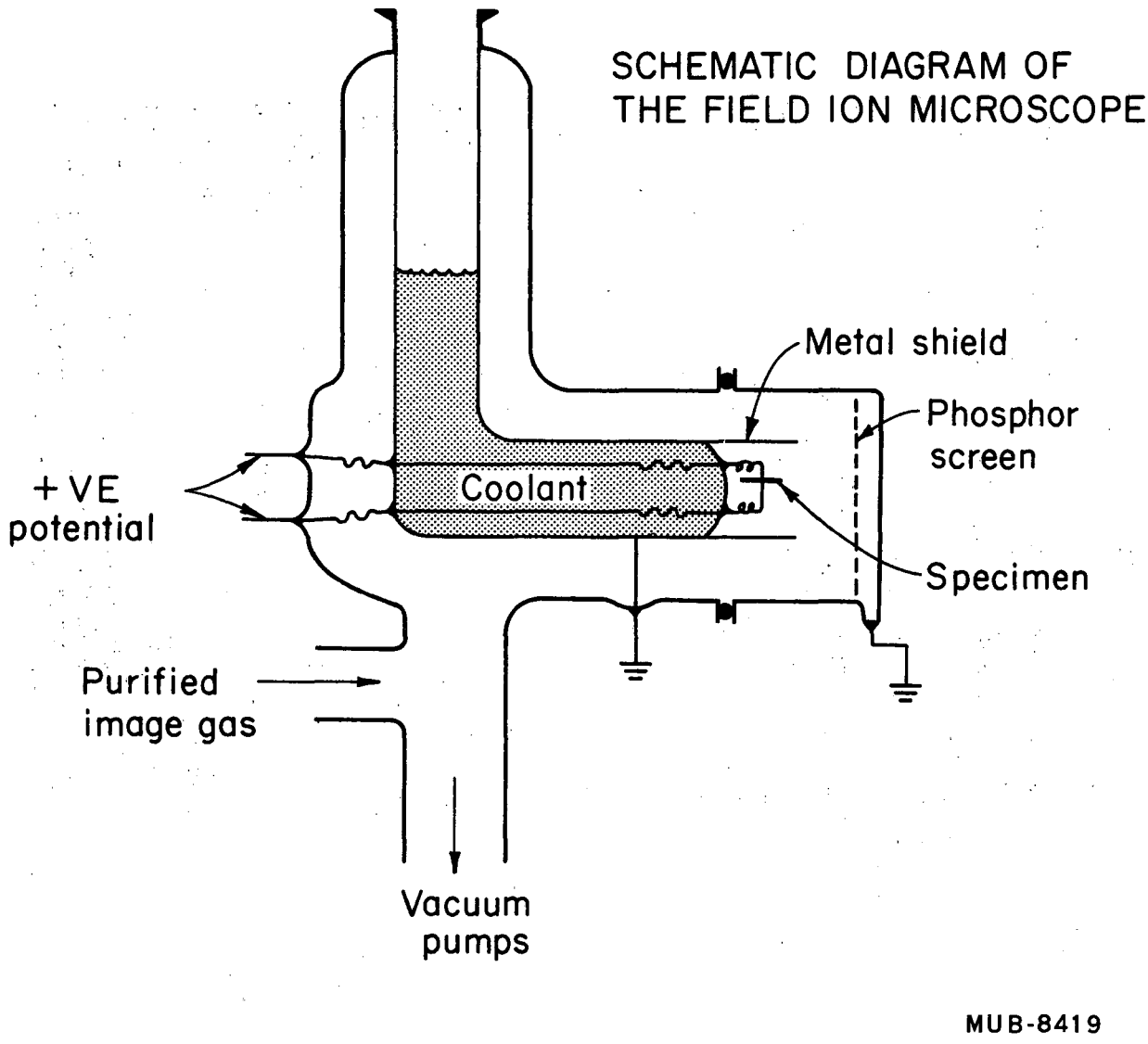
SCHEMATIC DIAGRAM OF
THE FIELD ION MICROSCOPE
Metal shield
Phosphor
screen
+ VE
potential
Coolant
Specimen
Purified
image gas
Vacuum
pumps
MUB-8419

Fig. 1

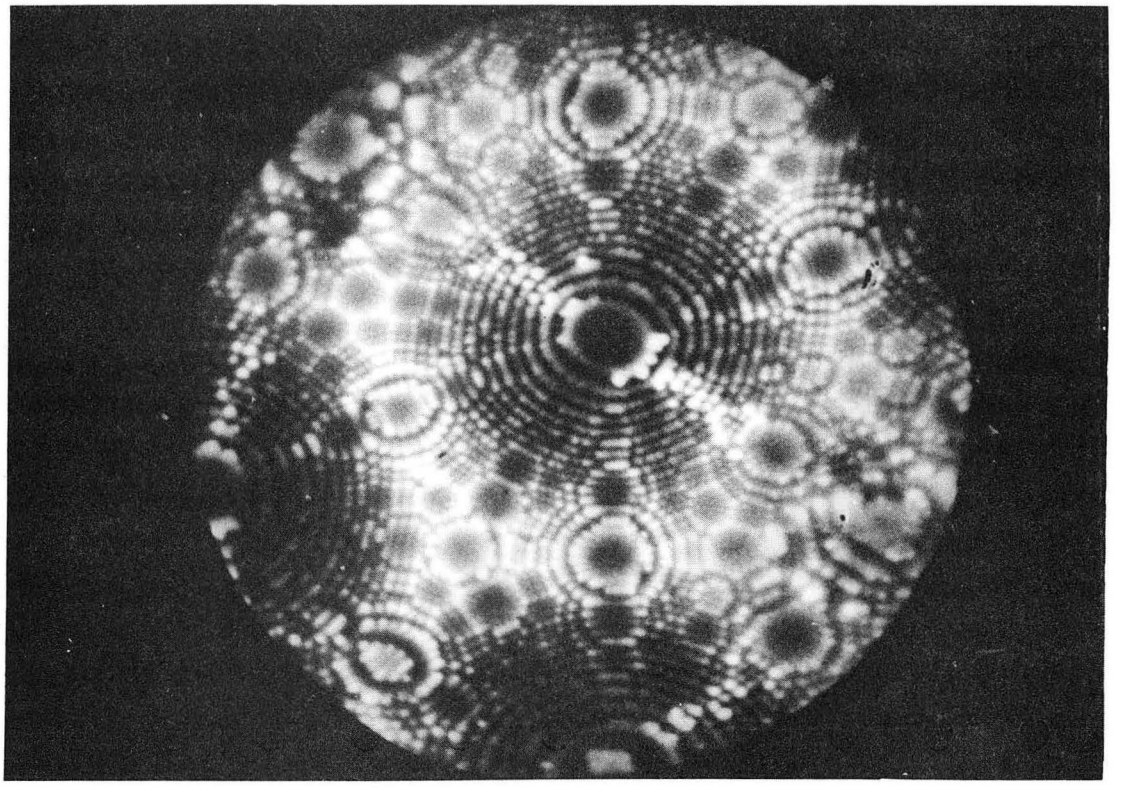

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Fig. 2

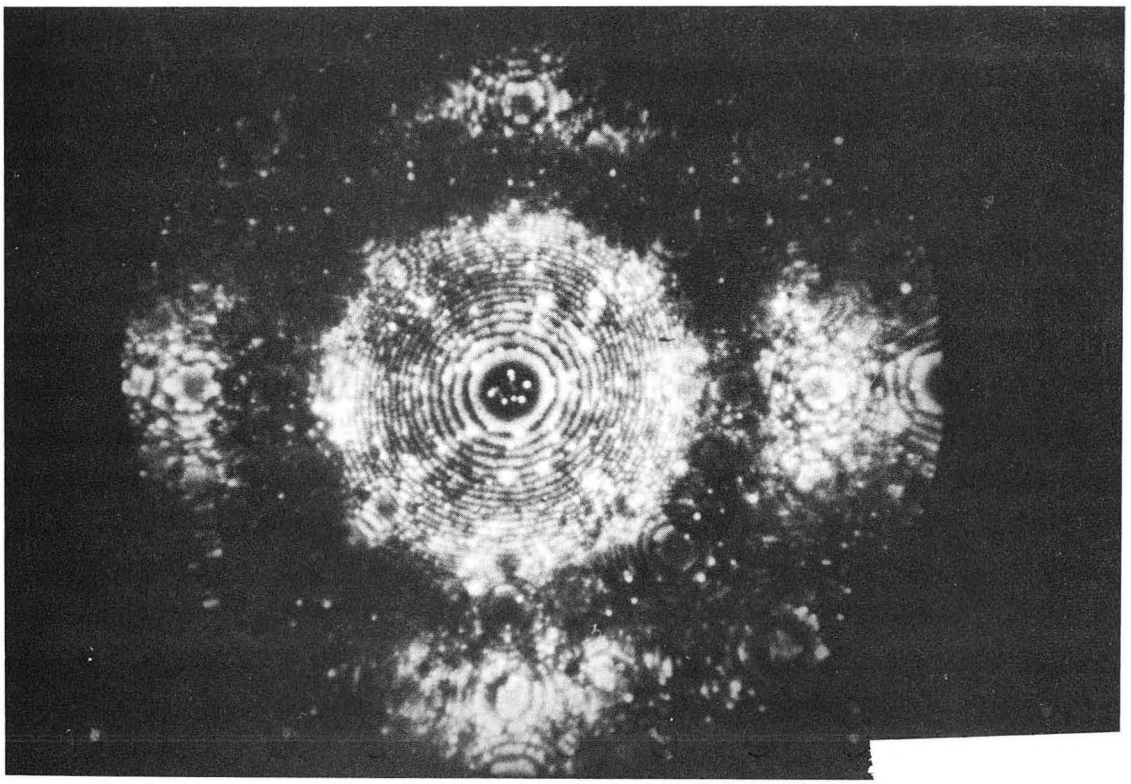

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Fig. 3

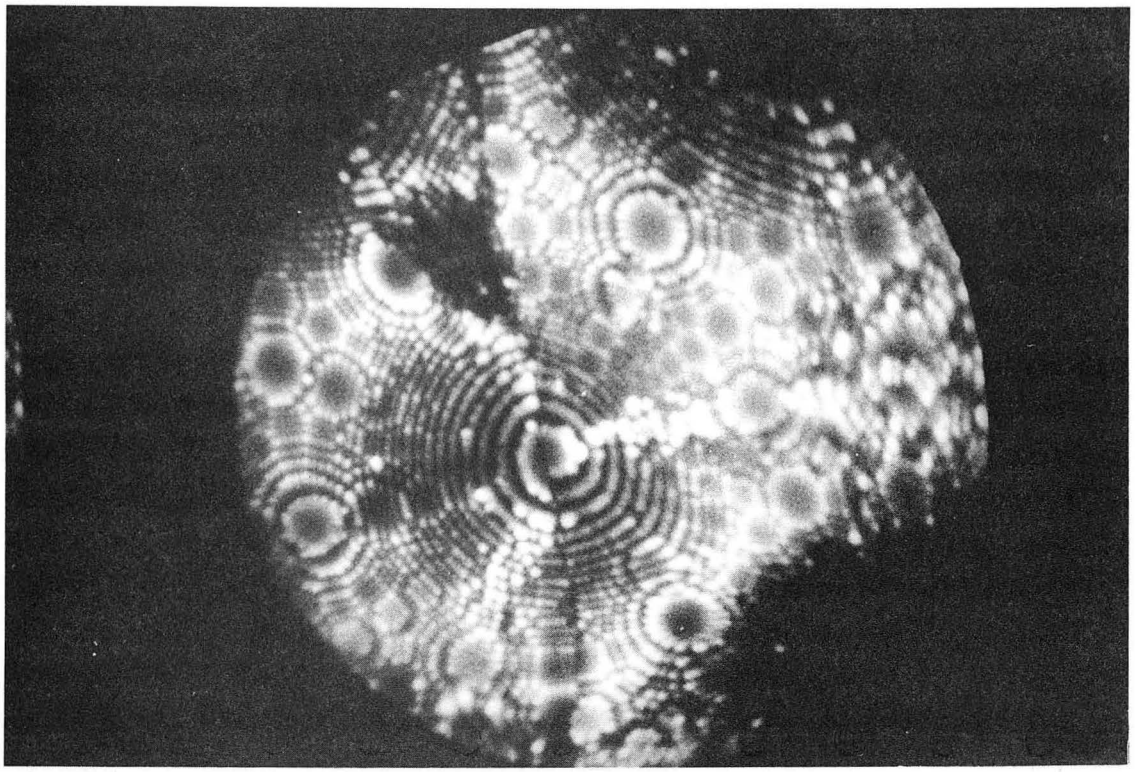

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Fig. 4

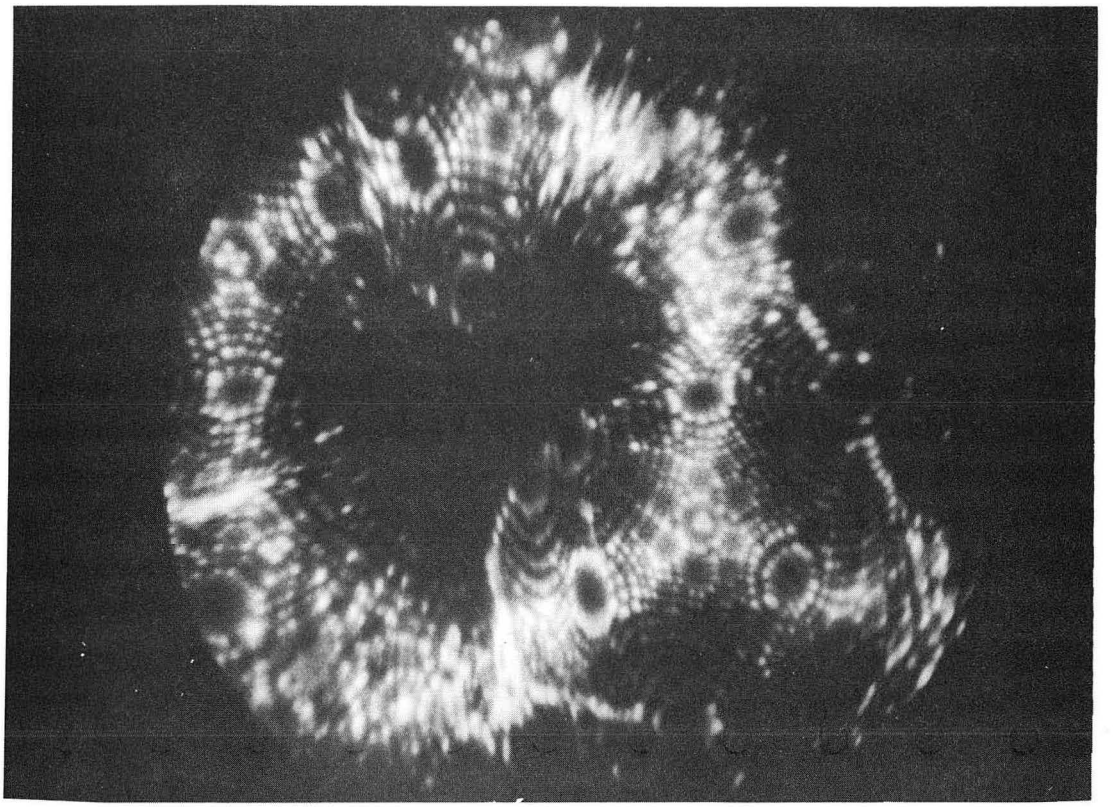

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Fig. 5

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