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MICROSTRUCTURE AND MAGNETO-ACOUSTIC OSCILLATIONS OF (CU, CO) NICKEL FERRITE

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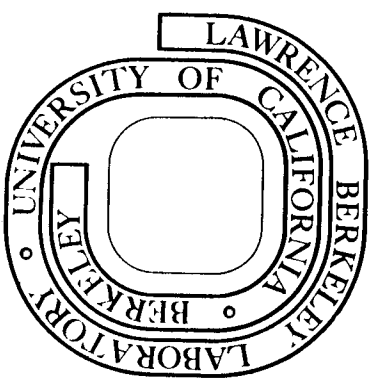

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MICROSTRUCTURE AND MAGNETO-ACOUSTIC OSCILLATIONS OF (Cu, Co) NICKEL FERRITE

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ABSTRACT

Effects of the microstructural features as revealed by scanning and transmission electron microscopy on the magnetostrictive vibration of Cu and Co doped $NiFe_2O_4$ are studied. Results show that changes in the grain size are strongly coupled with the geometry of the pores and the two features are not separable. The magneto-mechanical coupling coefficient is seen to depend strongly on the grain size. However, it appears that the pore structure and not the grain size is the important microstructural parameter that affects this magnetic property. Additional evidence is presented to show the importance of the pore geometry. Effects of microstructural features such as stacking faults, dislocations, nickel phosphide precipitates on grain boundaries, etc. are shown to be secondary in importance.

I. INTRODUCTION

In the area of microstructure-property relationship in magnetic materials, metallic alloy magnets have been investigated in great detail[1,2]. Only recently are ceramic magnets beginning to receive some attention[3,4]. With the introduction of modern metallographic techniques, some of the original problems of examining ceramic microstructures have been overcome and new areas of research have become possible[5]. In this paper, an investigation of microstructure and magnetostrictive oscillation properties of substituted nickel ferrite are discussed.

Ferrigmagnetic materials are suitable for use in magnetostrictive oscillators that can deliver high power in the ultrasonic frequency range. Efficient conversion of electromagnetic energy to mechanical energy by this method puts stringent requirements on

the magnetic, mechanical and magnetomechanical properties of materials[6]. Some ferrimagnetic spinels[7] (particularly nickel ferrite doped with small amounts of cobalt) have been shown to be well suited for use at moderately high frequencies. In these materials, the desirable properties such as high magnetostriction, low sensitivity to temperature variations[7], large magnetomechanical coefficient, etc. have been believed to be due to their chemical composition. The possible role of the microstructural features on the magnetostrictive oscillation properties is the subject of the present investigation.

II. EXPERIMENT

The ferrite specimens were prepared by solid state sintering[8]. The starting powder composition was 51.5 mole/o of Fe_2O_3, 41.4 mole/o of NiO, 6.75 mole/o of CuO, and 0.35 mole/o of $Co(NO_3)_2 \cdot 6H_2O$. Cu was added to enhance densification[7]. These were mixed, calcined, cold pressed and then sintered in air as well as in one atmosphere of oxygen for two hours at 1300°C in a platinum boat.

Specimens for examination in the scanning electron microscope were prepared from the sintered rods by etching thin slices of the material in hot H_3PO_4 for 10 minutes at 190°C. These were gold coated and examined in JSM U3 scanning microscope. Specimens for transmission electron microscopy were prepared by cutting 3 mm discs from the sintered material. These were then thinned first mechanically to a thickness of ~0.5 mil and finally by ion bombardment[5] until electrontransparent. The thin foils were examined in Hitachi HU-650 high voltage electron microscope operating at 650 kV.

A hybrid transformer impedence bridge was used for the impedence measurements and the magnetomechanical coupling coefficient was evaluated using the method described by Davies and Ferebee[9]. The specimens were in the form of toroids designed for a radial resonance frequency of ~40 kc. A comparison of the power delivery efficiencies of different materials were made by using a standardized magnetostrictive transducer geometry which was kept unchanged.

III. RESULTS AND INTERPRETATION:

When the cold pressed bars are sintered in air or in an oxygen atmosphere, the overall structure of the bar is as sketched in figure 1 with grain growth starting at the three exposed surfaces of the bar. The growth front propagates inwards to reduce the total

grain boundary area. However, examination in transmission and scanning electron microscopes reveal no detectable change in the porosity with grain growth. This is further confirmed by density measurements. Figure 2 is a scanning micrograph showing the interface between the large and small grain size areas. The interfaces have been etched away to reveal the individual grains. The small grains are faceted which could be due to selective etching of atomic planes[10].

The internal substructure of the material as revealed by the transmission microscope shows that the bulk material is single phase and most of the grains are free of structural defects. However, stacking faults in the cation sublattice[11] and isolated dislocation networks are occasionally seen as in figure 3. The grain boundaries are mostly incoherent and only rarely semicoherent. Very small pores ($\lesssim 1\mu$ in diameter) are present at the boundaries and grain corners. Although the porosity of the material does not change with grain growth, the shapes of the intragranular pores change significantly from spherical to a polyhedral shape (figure 4). In addition, many fine pores are detected in the transmission electron microscope that are not resolved in the scanning microscope. The average grain size in the interior depends on the sintering temperature. Pore geometry is seen to depend on the average grain size and not on the total porosity.

The grain growth can be eliminated completely by sintering the material with a packing powder of the same composition. However, the pore geometry does not remain spherical in all cases. A large grain size is always associated with the faceted pores and vice versa. It is also observed that octahedral precipitates of nickel phosphide form near the exposed surfaces of the samples during sintering and segregate on the grain boundaries as in figure 5. The density of these particles decrease with increasing distance from the surface. Since the particles do not form when the packing powder is used this could be due to contamination during sintering.

The magnetomechanical coefficient α (k_{eff} in reference 9) depends on the average grain size and is highest for the fine grain porous materials. The dependence is plotted in figure 6. The power delivery efficiency shows a similar dependence. The presence of nickel phosphide in the air or oxygen sintered specimens has no significant effect on α. Also the total pore volume does not affect α if the grain size is kept constant and porosity below 20%. Hysteresis curves for these specimens are shown in figure 7. The hysteresis loop changes with grain size, the coercivity being lowest for small grain size materials.

IV. DISCUSSION

From the results presented thus far, the difference in the values of α for small and large grain materials is quite large. Also, the result that small grain size materials have a smaller coercivity is contrary to what one might expect from a consideration of grain boundaries acting as barriers to the domain wall motion[12]. Apart from the grain sizes, the difference in the microstructures as revealed by high voltage electron microscopy is the pore geometry. In large grain materials, the pores have a polyhedral shape whereas they are nearly spherical in the small grain materials. Since large grain structures are associated with higher sintering temperature, ease of mass transport and anisotropy of surface energy[10] result in the polyhedral pore geometry. The inhomogeneity represented by such pores may give rise to higher coercivity if the plane of the domain wall coincides with that of a pore wall, (as a result of more effective pinning). The small value of α for large grain materials might be due to the associated pore geometry and not the grain size as presented in figure 6. A systematic study of effect of pore structure on magnetostriction and other magnetic properties is necessary to fully evaluate the effect of pores as a microstructural feature of the sintered or hot pressed ceramic magnets. The observation of the insensitivity of the value of magnetomechanical coefficient to porosity (below 20%) is contrary to the results reported in the literature[14] (which could have been due to a change in the pore structure).

The effect of the low concentration of structural defects is difficult to evaluate. Cation stacking faults, when present in large density, may interact with planar domain walls and influence the dynamic magnetic properties. The effect of the nickel phosphide on α is seen to be negligible and has not been investigated further. Also, the effect of a second phase in this ferrite could not be studied since no phase decomposition through a solid state phase transition occurs at this composition.

Properties of ceramic magnets have long been controlled by varying chemical composition and other processing variables. However, due to lack of microstructural information of the product materials, role of the microstructural variables has gone unnoticed. The above results and works of earlier investigators[4] indicate the important role played by the microstructural features on the magnetic properties. A better understanding of these characters may lead to desirable processes and materials for various applications.

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FIGURES

Fig. 1 Sketch of the cross-section of a sintered bar. (1) large grain size outer layer (2) small grain size core (grain diameter $\lesssim 1\ \mu$) and (3) the surface of the rod resting on platinum boat during sintering.

Fig. 2 Scanning electron micrograph showing the etched surface of the sintered bar. I-I is the interface between the small grain and large grain regions. Note the faceted pores in large grain region and the faceted small grains.

Fig. 3 Transmission electron micrograph showing (a) cation stracking faults and (b) dislocation network in the sintered materials. The cation fault is of $\{110\}\frac{1}{4}\langle 110\rangle$ type and the dislocations have a Burgers vector $\frac{1}{2}\langle 110\rangle$.

Fig. 4 Transmission electron Micrograph showing the geometry of pores in a) small grain material and b) large grain material.

Fig. 5 Scanning electron micrograph of the outer surface of a sintered bar. The precipitates (p) on the boundary are nickel phosphide as confirmed by EDAX and HVEM.

Fig. 6 Plot of magnetomechanical coupling constant (α) vs. average grain diameter. The nickel phosphide precipitates are present only in specimens corresponding to point A. C and B correspond to the interior of the rods sintered at different temperatures.

Fig. 7 Magnetic hysteresis curves of the sintered bars. A, B and C correspond to those of Fig. 6 above.

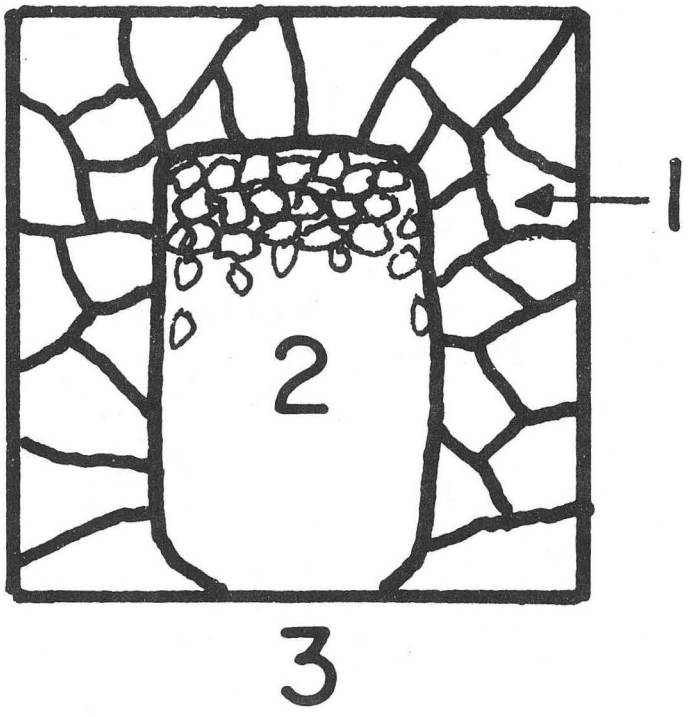

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FIG. 1

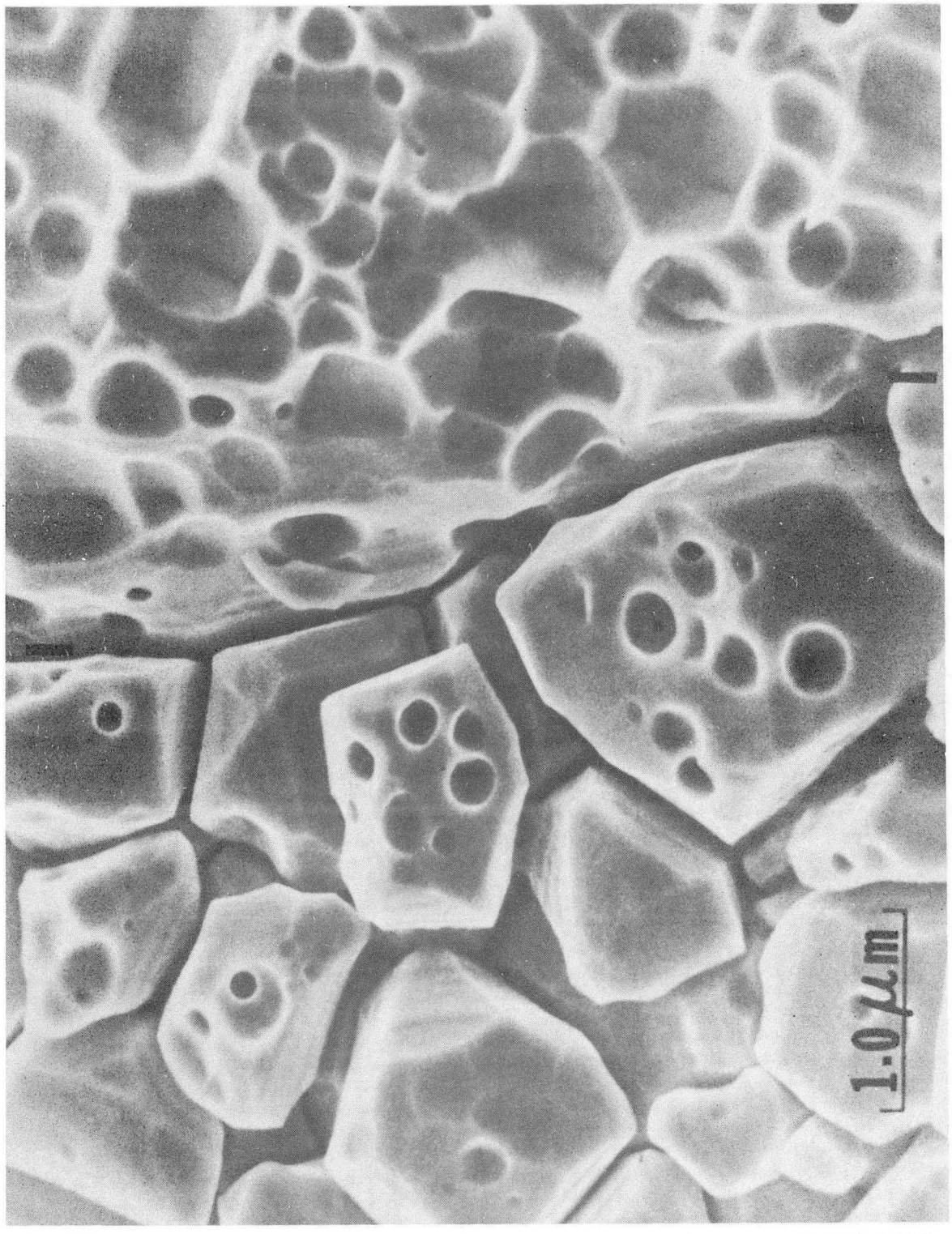

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FIG. 2

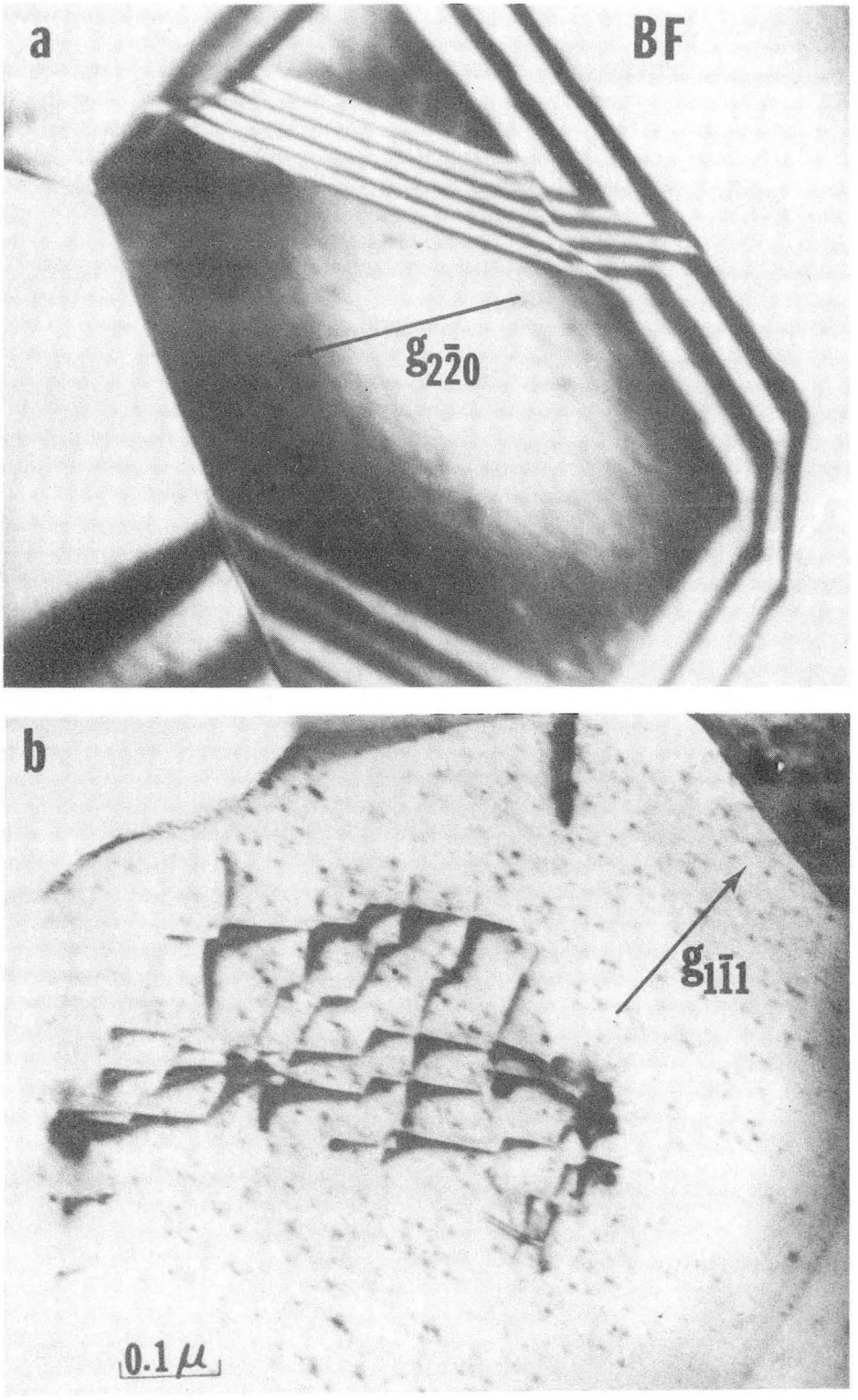

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FIG. 3

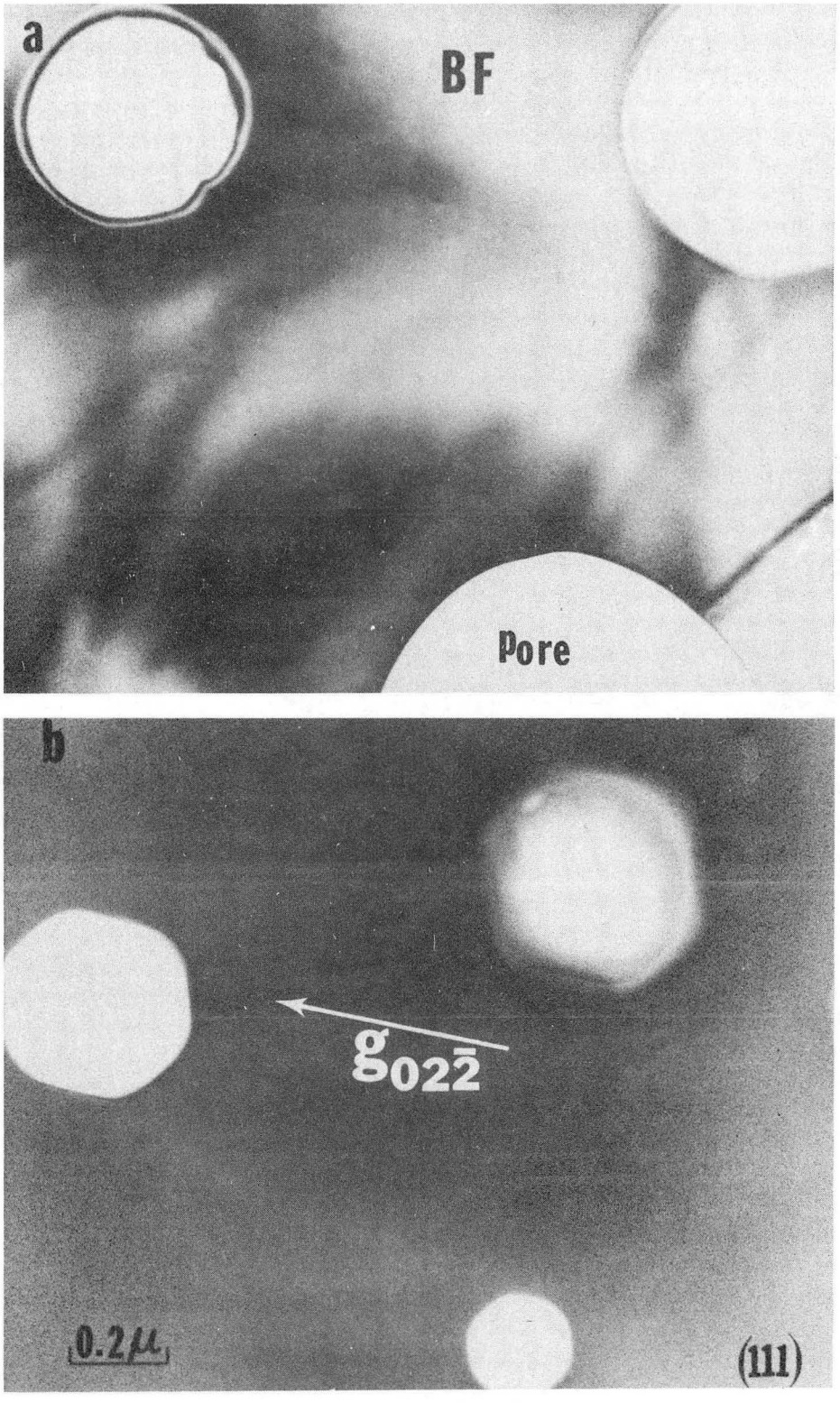

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FIG. 4

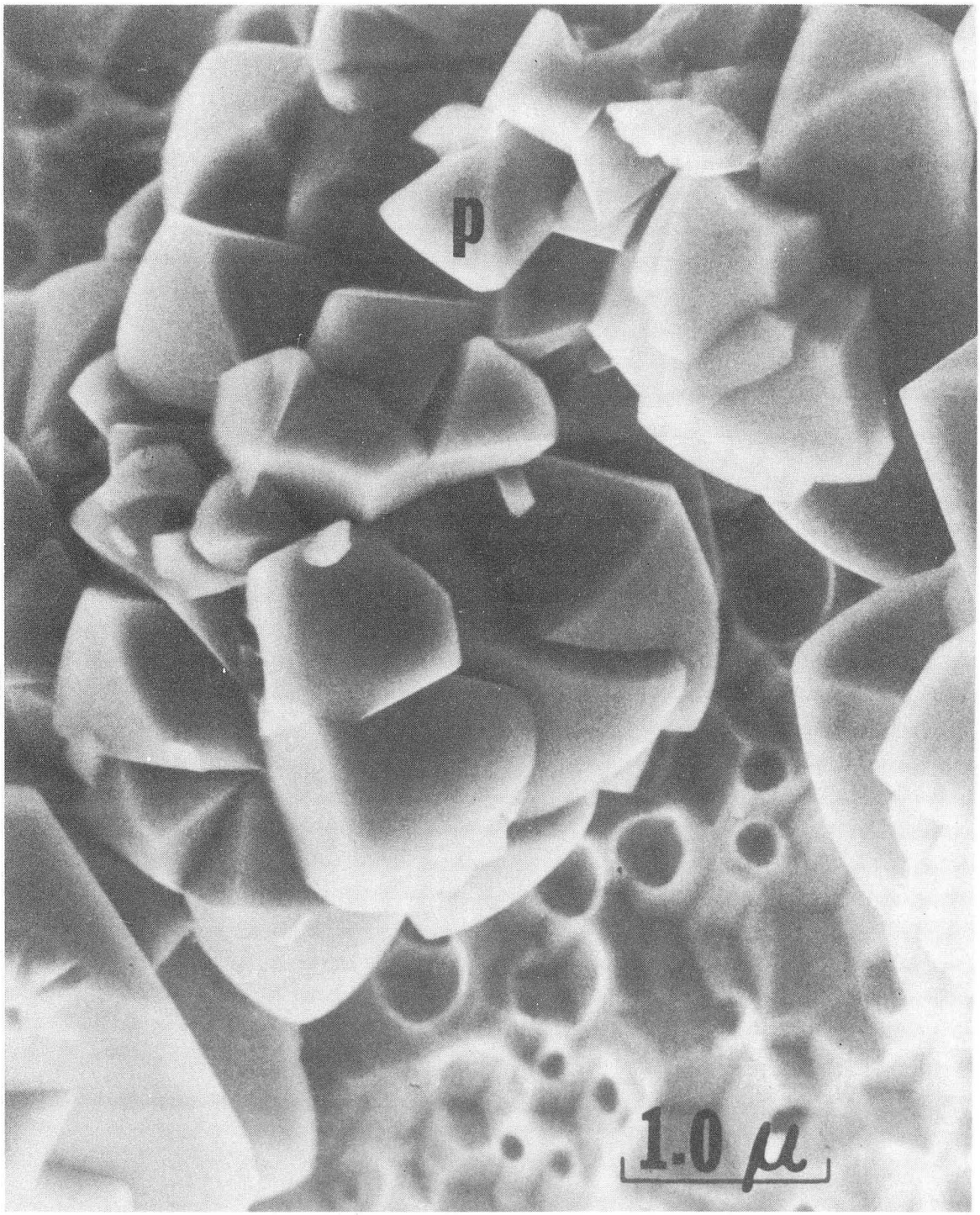

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FIG. 5

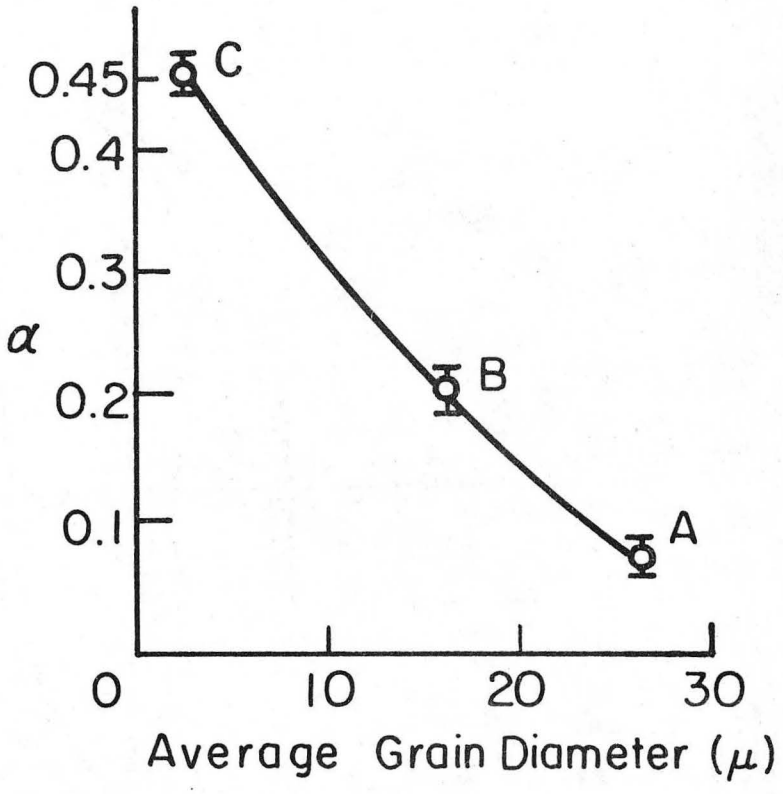

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FIG. 6

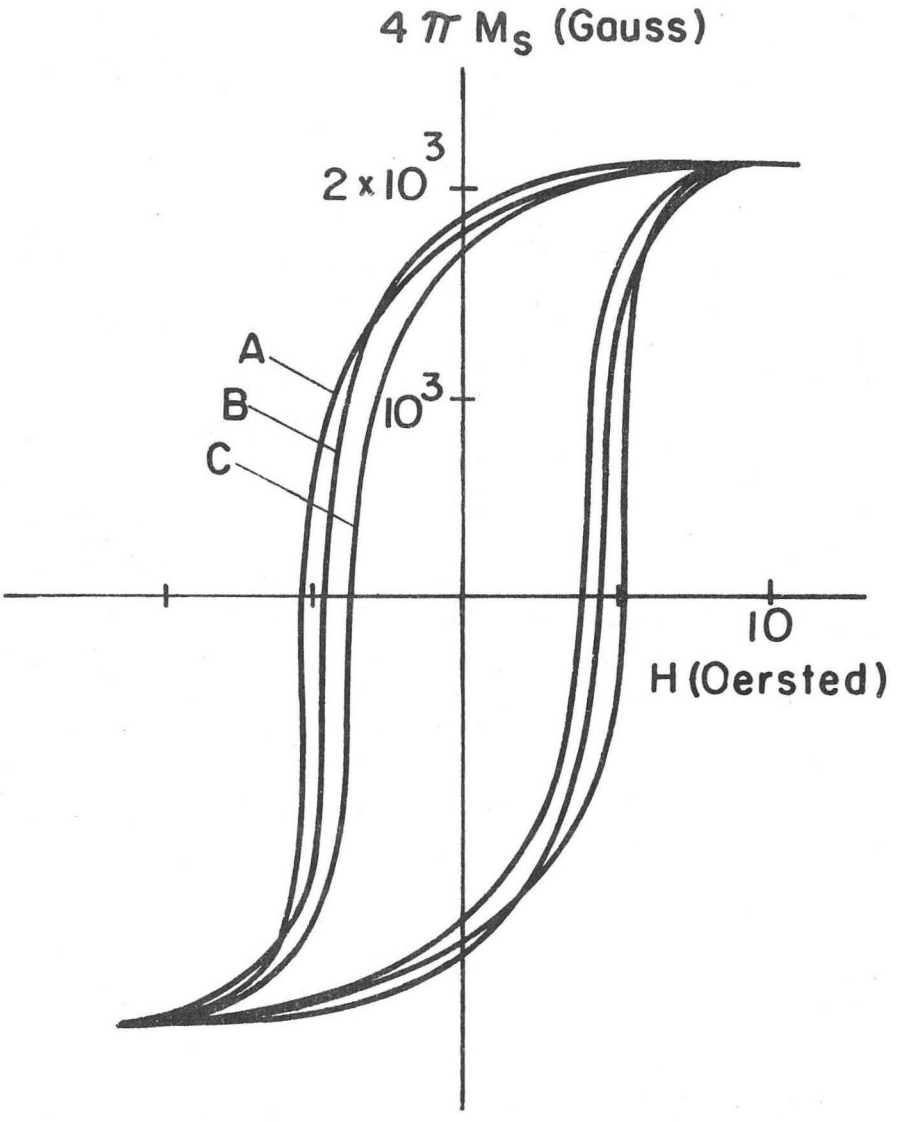

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FIG. 7

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