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H.-M. Ho, E. Goo, and G. Thomas

July 1985

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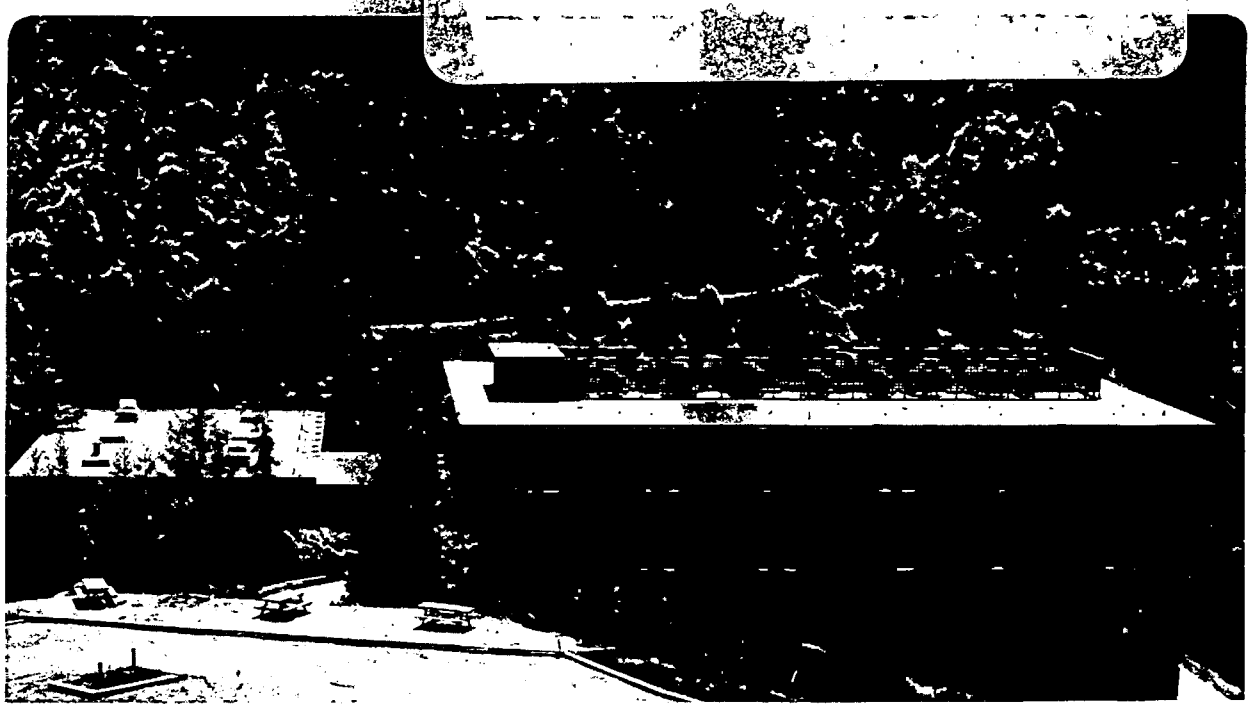

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Crystal Structure of Acicular γ-Fe_2O_3 Particles Used in Recording Media

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Abstract

γ-Fe_2O_3 particles have been examined by convergent beam electron diffraction to determine the crystal symmetry. The particles have a primitive lattice with an m3m point group and a cubic superstructure with lattice parameter approximately equal to three times the lattice parameter of the magnetite structure. This superlattice is a result of cation vacancy ordering. An order-disorder transition of the structure is observed in the electron microscope and is believed to be caused by electron radiation-enhanced diffusion.

Introduction

γ-Fe_2O_3 particles were developed more than half a century ago and today it is still the most widely used magnetic material for disks and tapes. γ-Fe_2O_3 is commonly prepared via the conversion of αFeOOH or γFeOOH to Fe_3O_4, by heating and reduction, followed by oxidation of the Fe_3O_4 to γ-Fe_2O_3. Fe_3O_4 which has a cubic inverse spinel structure converts to γ-Fe_2O_3 by removing 8/3 Fe ions per unit cell. Because of its application as magnetic recording media, the structure of the material has been studied by many investigators. However, due to the fact that (1) the structure contains large amounts of cation vacancies so that it is sensitive to the environment, (2) the small particle size, and (3) the difficulty in growing single crystals for X-ray determination, unambiguous result for the structure have not yet been obtained.

Thus, it is the object in this study to utilize convergent beam electron diffraction (CBED) so as to allow examination of individual particles to be done so as to determine their crystal structure.

Experimental

In the present study, two commercial γ-Fe_2O_3 samples from different sources[1] were obtained. Samples from the audio tapes were prepared by removing the plastic substrate with acetone solution and ion milling the magnetic

coating until it was electron transparent. Samples from the powder particles were prepared by dispersion on a carbon film coated electron microscope grid. The particles examined were about 0.2 - 0.45μm in length and with a length/diameter ratio of about 5. All microscopy and microdiffraction (CBED) was performed in a Philips EM 400 at 100 kv. A liquid nitrogen cold stage was used to acquire sharp CBED patterns and to avoid rapid contamination of the particle under the convergent beam. The convergent beam was about 400Å in diameter so allowing direct observations to be made of individual particles.

From a CBED zone axis pattern, crystal symmetry information can be obtained by observing the high order Laue zone (HOLZ) symmetry and by observing the internal structure of the zero order discs. Point group determination[2] requires precise examination of the diffraction pattern symmetry and reference to the tables published by Buxton et. al.[3] Space group determination can be achieved by observing the presence of the so-called line of dynamic absence which occurs in kinematically forbidden reflections and is related to the presence of a screw axis or a glide planes[4].

Results and Discussion

Table 1 is a summary of previously published results[5-15]. It is not surprising that these results are not consis-

tent because the techniques employed can only provide average data of the material. Among the results, it is generally believed that γ-Fe_2O_3 has a tetragonal structure of c/a = 3 with a = 8.33Å[12] due to the fractional nature of iron cation vacancies.

X-ray data obtained in the present research were similar to those referenced in Table 1. As shown in Fig. 1, several non-magnetite extra lines such as 110, 210, 211 etc. were found. These extra lines indicate a reduction in symmetry from a face-centered lattice to a primitive lattice has occurred. This finding is also supported by electron microdiffraction results, as shown in Fig. 2, in which reflections forbidden by the fcc structure such as 100, 110, 210 etc. are allowed. For convenience, Fig. 2 is indexed in terms of a Fe_3O_4 unit cell.

Figs. 3 and 4 are primary CBED zone axis patterns of the same specimens as used for X-ray analysis. Both γ-Fe_2O_3 samples clearly showed the same crystal symmetry. Since the internal structure of the discs can not be seen, the crystal symmetry must be determined from analysis of the HOLZ symmetry. As shown in Fig. 5, the HOLZ symmetry is more easily resolved when smaller condenser lens apertures are used (e.g. 50μm). From Fig. 5, it can be seen that the <100>, <110> and <111> zone axis patterns show the 4mm, 2mm and 3m symmetries, respectively. From tables published by Buxton et. al[2] the point group can be unambiguously determined to be m3m. This means that

vacancies are ordered in such a way that the unit cell remains cubic. This crystal symmetry also rules out all of the space groups proposed by previous investigators[5,11,12]. Due to the small particle size, no structure is visible in the zero order reflections and the space group of the material can not be determined. However, from the knowledge that γ-Fe_2O_3 has a primitive lattice and m3m point group, there are only 4 possible space groups: Pm3m, Pm3n, Pn3m and Pn3n.

The spacing between layers, H, in the reciprocal lattice can be calculated from the CBED pattern as

$$H = K - K\sqrt{1 - (R/L)^2}$$

where K is the reciprocal of the incident electron wavelength, R is the radius of high order laue ring, and L is the camera length.

By using above equation, the γ-Fe_2O_3 unit cell is consistently derived from all three primary zone axis patterns to be cubic with lattice parameter approximately equal to three times that of the magnetite lattice parameter. Fig. 6 is a series of CBED <110> patterns taken from the same area of a particle during prolonged exposure. Under the convergent electron beam, the ordered structure with lattice parameter of 25Å is observed to gradually change to a disordered structure with lattice parameter of 8.33Å. This result suggests disordering has occurred so that vacancies are no longer evenly distributed in each unit cell.

Similar order-disorder transitions have been observed in <100> and <111> zone axes as well and the resultant structure continues to have the m3m point group symmetry, as shown in Fig. 7.

The same pattern as Fig. 6(f) is obtained after re-examining the same area also in a liquid nitrogen cold stage several days later. This result confirms that the order-disorder transition is not due to local specimen heating by the electron beam.

Furthermore, at 100 kv, knock-on displacement damage is not likely to take place in an ionic material[16]. However, electrons may transfer, by ionization damage, sufficient momentum to enhance cation diffusion, especially in a high defect density material such as γ-Fe_2O_3. In such cases the activation energy required for cation diffusion is low so that diffusion may be enhanced by electrons of energy even less than 100 kv[16]. Thus, the mechanism of this order-disorder transition is considered to be due to radiation-enhanced diffusion of cations in the electron beam. No attempt has been made in this work to measure this quantitatively.

Conclusion

Because of the difficulties in obtaining information directly from individual particles, there are many discrepancies in the literature regarding the structure of

γ-Fe_2O_3 particles. In this study, whereby individual particles have been examined by electron microscopy and microdiffraction, the following conclusions have been made:

(1) γ-Fe_2O_3 particles prepared for commercial audio tapes have a primitive cubic lattice and m3m point group, therefore the space group of the material can only be one of four possible space groups.

(2) The material has a cubic superstructure of lattice parameter 25Å as a result of cation vacancy ordering.

(3) Order-disorder transition occurs by electron irradiation during observation. This transition is probably due to enhanced diffusion by ionization damage.

Acknowledgements

The authors would like to thank TDK company of Japan and Hercules Incorporated for supplying the γ-Fe_2O_3 particles used in this study. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U. S. Department of Energy under contract No. DE-AC03-76SF00098.

Figure captions

Figure 1. X-ray diffraction traces of γ-Fe_2O_3 showing several extra lines.

Figure 2. Microdiffraction patterns of γ-Fe_2O_3 from (a) <100> and (b) <110> zone axis. Forbidden reflections for the fcc structure such as 100, 110, 210 etc. are allowed indicating the lattice is a primitive cubic.

Figure 3. CBED zone axis patterns from tape samples showing a cubic threefold superstructure, (a) <100>, (b) <110> and (c) <111> pattern.

Figure 4. CBED zone axis patterns from powder samples also showing a cubic threefold superstructure, (a) <100>, (b) <110> and (c) <111> pattern.

Figure 5. CBED patterns showing m3m point group symmetry, (a) <100>, (b) <110> and (c) <111> pattern.

Figure 6. <110> CBED patterns showing a transition from a ordered structure (a) to a disordered structure (f). The time lapse (a)-(f) is approximately 40 minutes.

Figure 7. Zone axis patterns of disordered structure showing the structure continues to have the m3m point group, following structure disordering.

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Table 1. Published structural studies on γ-Fe_2O_3

Author	Technique	Vacancy Distribution	Space Group
Hagg[5]	X-ray diffraction	distribute uniformly in the cation sites	Fd3m
Verwey[6]	same as above	same as above	
Neel[7]	saturation magnetization measurement	only over the octahedral sites	
Ferguson and Hass[8]	neutron diffraction	only in the octahedral sites	
Haul and Schoon[9]	X-ray diffraction	vacancy ordering result in a primitive lattice	
Chaudron[10]	same as above	same as above	
Braun[11]	same as above	same as above	$P4_1$ with c/a=3
Van Oosterhout and Rooijmans[12]	same as above	same as above	$P4_132$
Ueda and Hasegawa[13]	X-ray and neutron diffraction	occupy only four of the 16d sites	
Takei and Chiba[14]	X-ray diffraction	no vacancy ordering	
Beudeulle et. al.[15]	X-ray and electron diffraction	either with noncubic symmetry or with cubic superstructure with a threefold unit cell	

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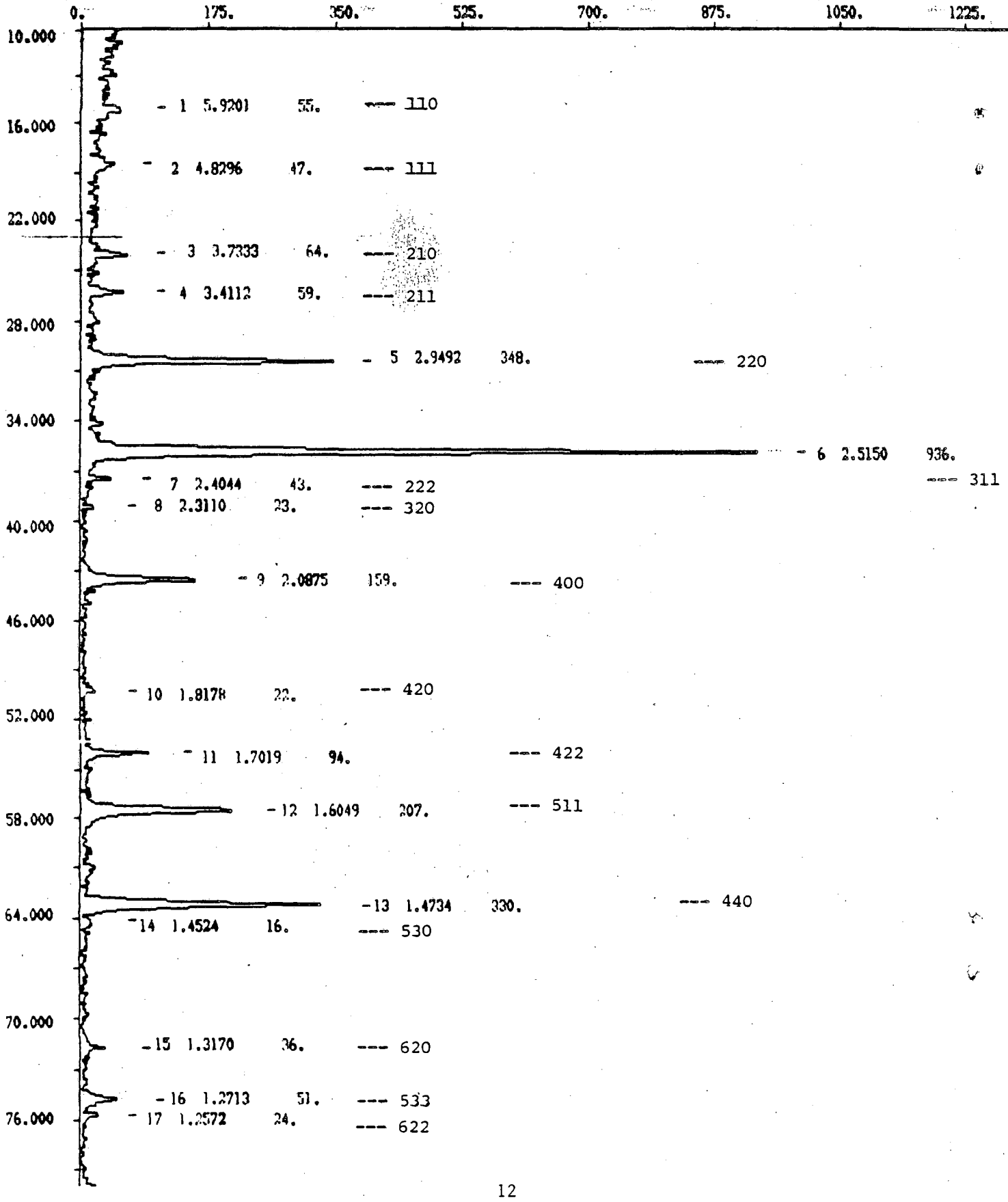

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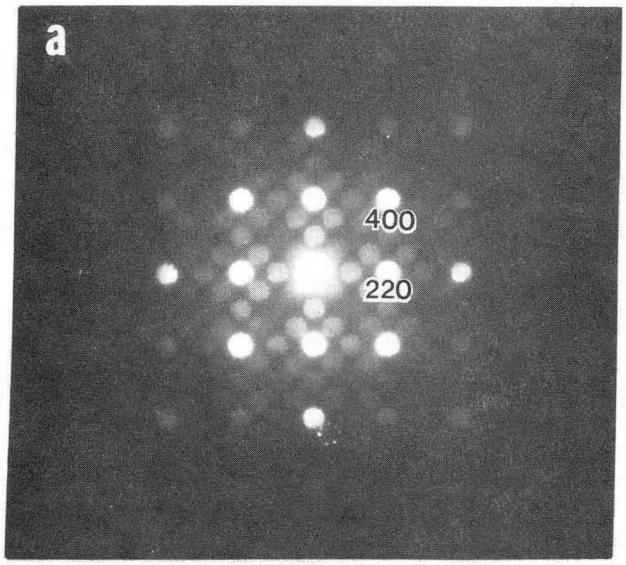
Fig. 1



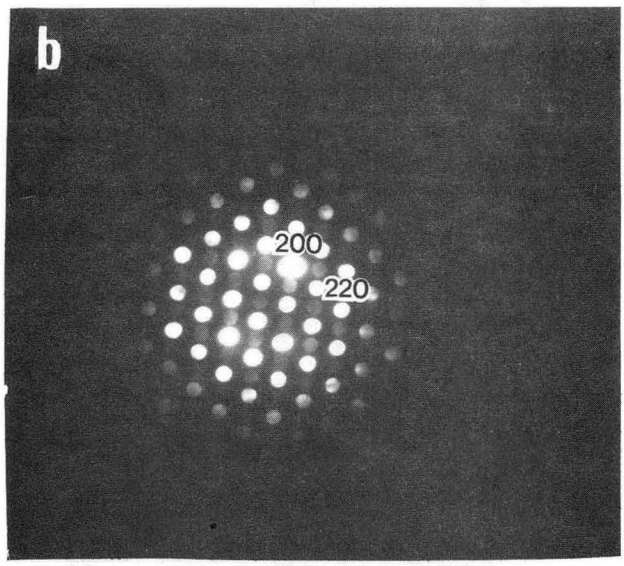


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Fig. 2

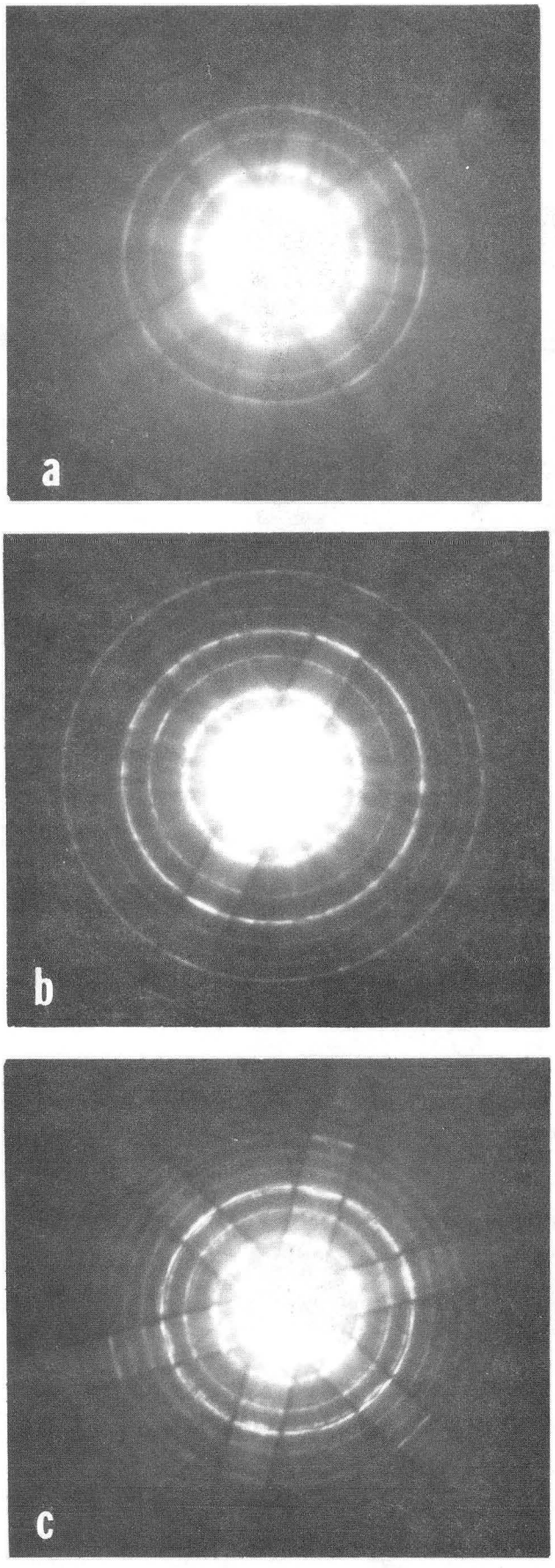

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Fig. 3

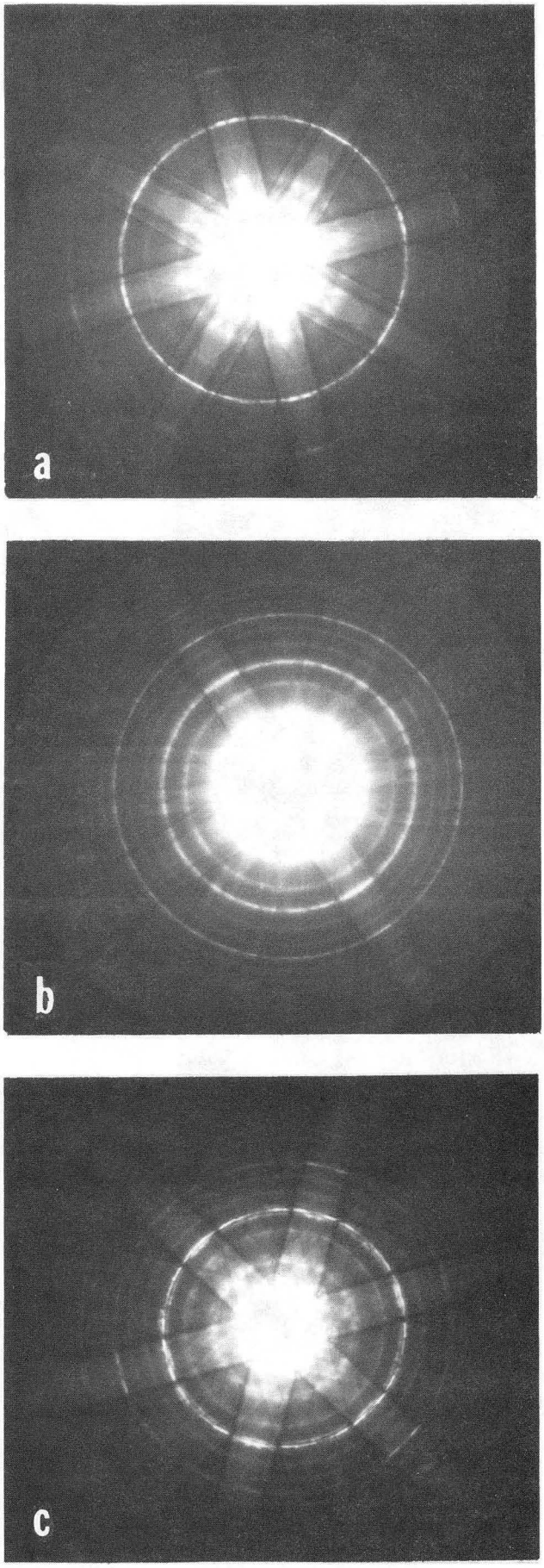

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Fig. 4

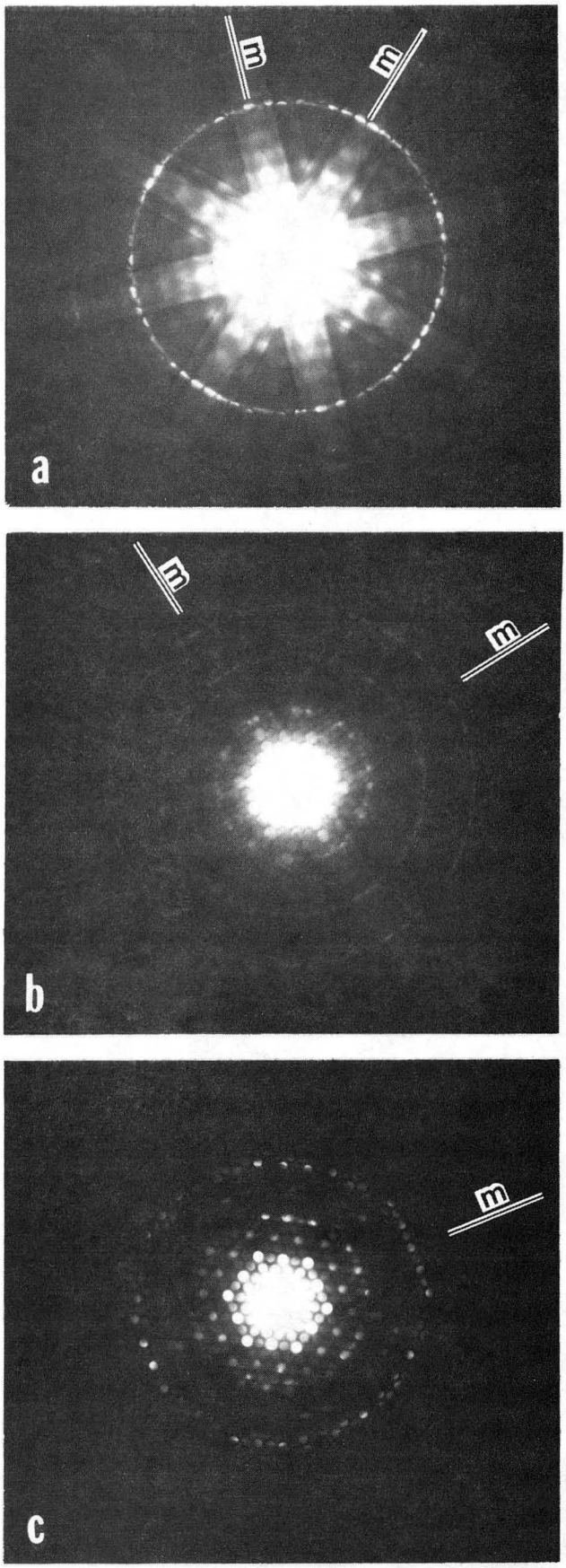

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Fig. 5

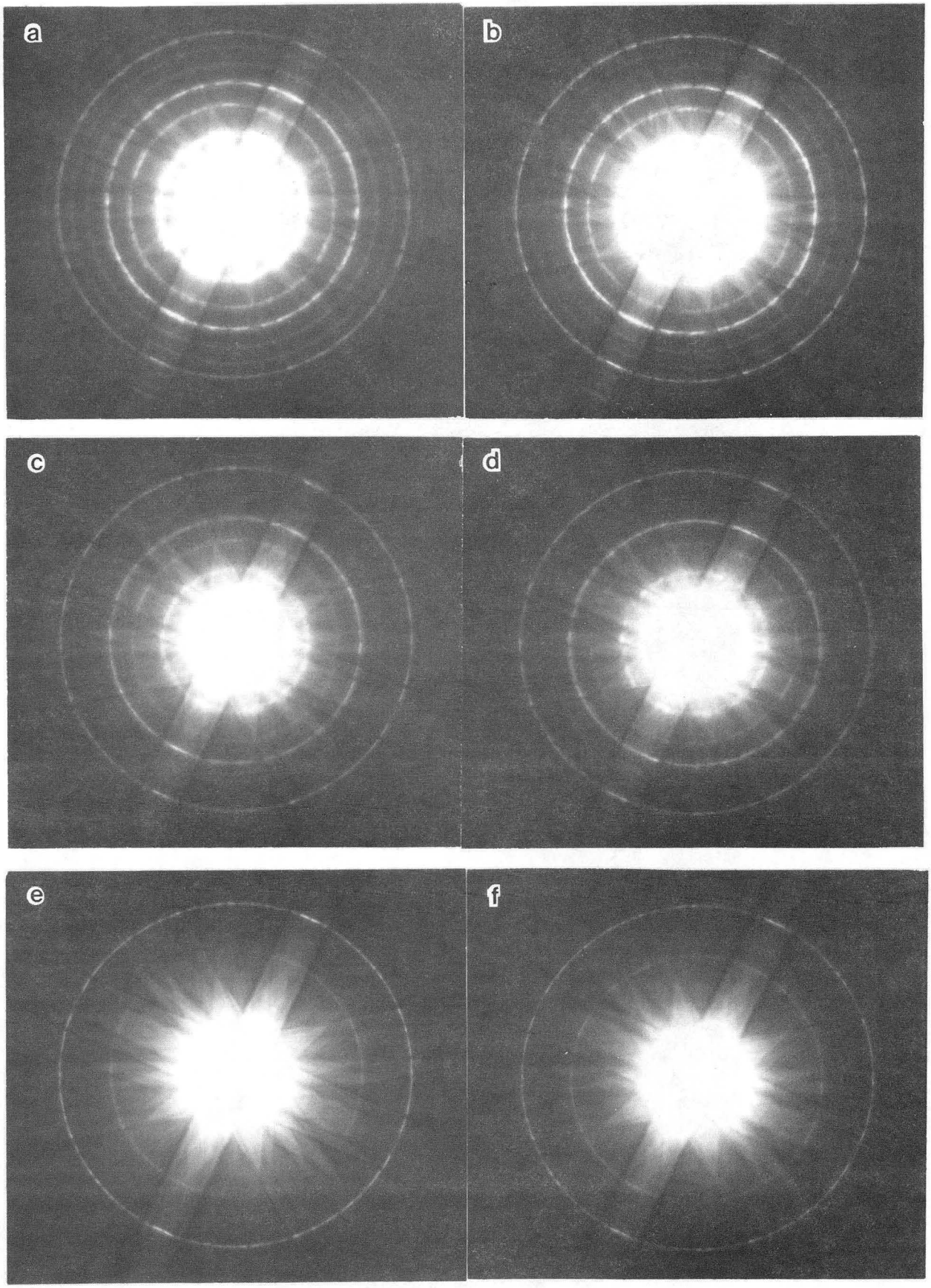

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Fig. 6

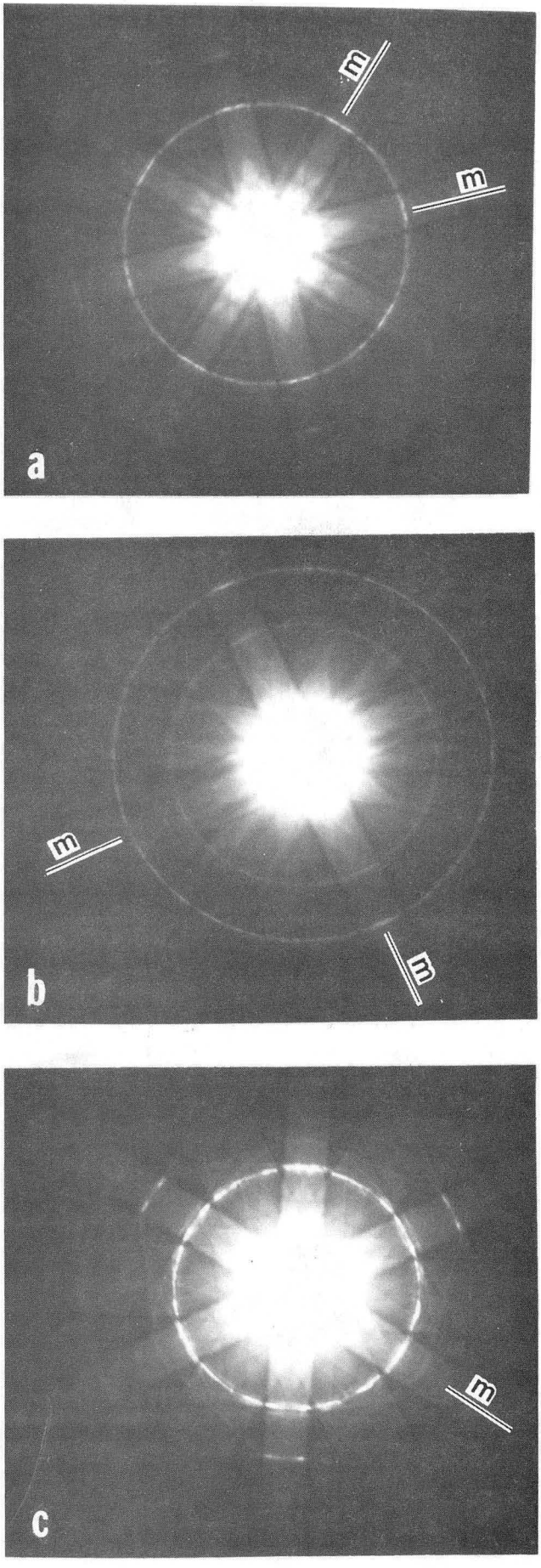

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Fig. 7

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