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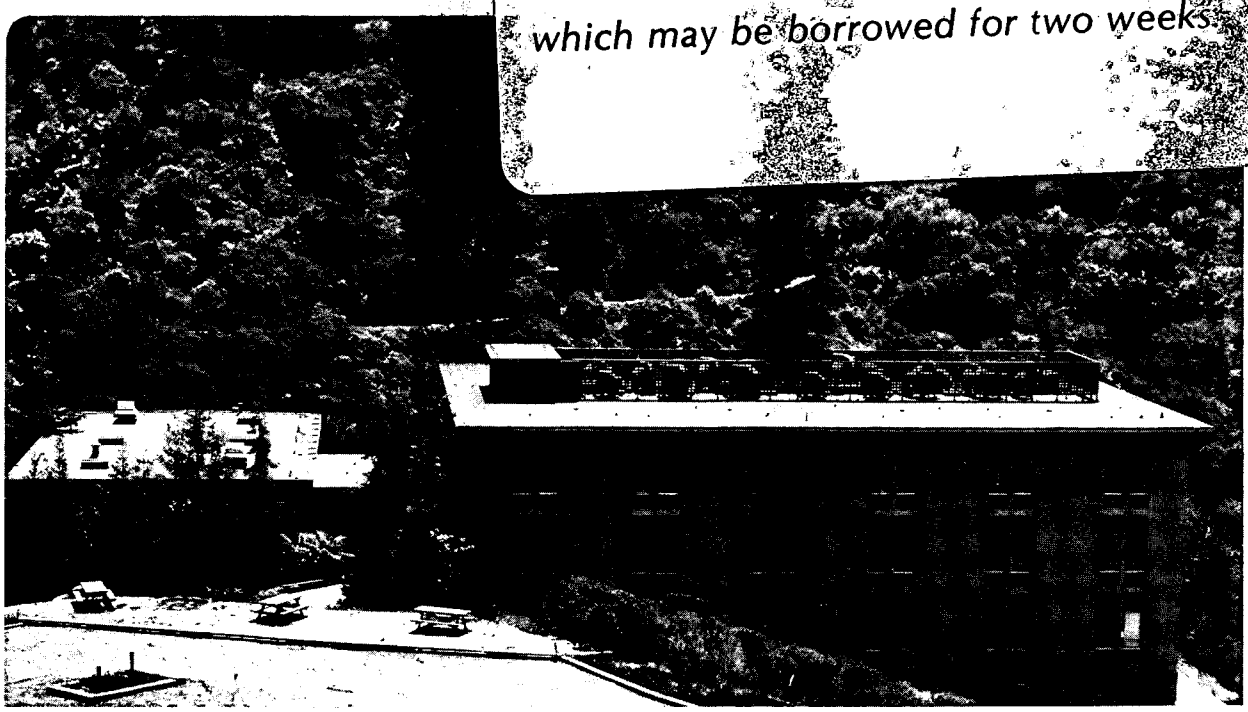

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MICROSTRUCTURE OF Fe-DIDYMIUM-B MAGNETS

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ABSTRACT : A TEM study has been made to characterize the microstructure and composition of the phases in the Fe-Didymium-B magnets. The main phase is the tetragonal $RE_2Fe_{14}B$ phase. In all the samples observed, a triple junction fcc phase which frequently extended into two-grain junctions, was observed with a lattice parameter of 5.24 A and enriched in Ce, Pr and Nd. The magnets with poorer properties had a considerable amount of the rare-earth oxide.

INTRODUCTION : The discovery by Sagawa et.al[1] of a new hard magnetic compound based on the Fe-Nd-B system has revolutionised the area of permanent magnets. Further improvements have reduced the cost of production of these magnets by the use of rare earth mixtures[2,3]. Specifically the addition of Cerium has been studied, since it is thought that this leads to better sinterability[3]. It is of interest to know the exact microstructural characteristics of this system and the role of each phase in the realization of the magnetic properties of the system. This is especially true in the explanation of the coercivity mechanism in this class of magnets. It is widely believed that the dominant mechanism is controlled by the nucleation of reverse domains[4,5,6]. The role, if any, of the fcc phase is still not clear. In this paper, the results of preliminary experiments on the Fe-Didymium-B system are reported, where Didymium refers to a mixture of Nd, Pr and Ce[2].

EXPERIMENTAL : The alloys were produced by standard processing techniques adopted, and are described elsewhere[2,3]. The alloys hada nominal composition of Fe-33.5wt.% RE-1wt.%B with the rare earth composition of 80% Nd, 15% Pr and 5% Ce. They were suitably heat-treated[2] to achieve coercivities and energy products in the range 3.7kOe to 8.9kOe and 24MGOe to 39.5MGOe respectively. From the buttons 500 microns thick foils were cut off which were then mechanically thinned down to about 75-100 microns and finally ion milled to electron transparency. The foils were examined in a JEOL 200CX AEM at 200kV, fitted with an

ultra-thin window detector, and in a Philips 400TEM/STEM microscope at 100kV. The microanalysis was carried out using the theoretical k-factors from the system software. Their validity was checked by comparing the composition of the matrix phase obtained from the analysis with the actual stoichiometric composition. Since the fit was within 2% of that reported in literature, the same theoretical k-factors were used in the subsequent analyses.

The analyses were carried out in the convergent beam mode with a probe size of 400A. To ensure good counting statistics, a 300 second counting time was used.

RESULTS AND DISCUSSION : The main emphasis in this paper is on the crystal structure and composition of the grain boundary phase. Sagawa et. al[1] reported it to be an fcc phase but Fidler and Yang[7] reported a dhcp structure. Hiraga et. al[10] reported that there was abcc phase at the two grain junctions. Thus a definitive determination of the crystal structure was thought necessary. Fig.1 shows the general structure with the fcc phase in bright contrast and the matrix appearing dark. [The microstructure within this phase is under investigation]. In some cases, this phase extended to two-grain junctions, and were also uniformly found to be the same fcc phase.

The <100> microdiffraction pattern of the grain boundary phase is shown in the inset as well as the EDX spectra of this phase and the matrix. To determine the crystal lattice uniquely, a set of

tilting experiments were carried out. Fig.2 shows a tableau of microdiffraction patterns from the grain boundary phase. While the presence of the <100> type pattern rules out the dhcp structure, the <110> type pattern rules out the bcc structure. The diffraction patterns can be consistently indexed as an fcc structure. The chemical analysis of this phase is given in Table I. Note that for the tetragonal phase, the Fe/RE ratio is very close to that in the stoichiometric $Nd_2Fe_{14}B$ phase. It has been suggested by Stadelmaier and ElMasry[8] that this phase could be stabilized by dissolved oxygen, since there is no fcc phase in the Nd rich portion of the Fe-Nd phase diagram. Referring to the EDX spectrum of the fcc phase in Fig.1, a small oxygen peak was barely discernible. If this was taken into account as a legitimate peak, then the analysis is different, [Table I]. Thus, our preliminary analysis was not conclusive. Further experiments are being carried out to determine the microchemistry of this phase with accuracy.

There is considerable partitioning of Ce and Pr to the grain boundary phase, Table I. Thus, one of the purposes of adding Cerium appears to be justified, in that Cerium partitions selectively to the grain boundary, thus providing an effective reaction path for the sintering to continue.

The samples with coercivities in the lower range, i.e., 3.7-6.5 kOe were looked into in greater detail. The analytical microscopy of these samples indicated the presence of the rare earth sesqui-oxide, as large independent grains, Fig.3. The large amount of oxygen is confirmed by the EDX analysis [TableI]. By a

similar set of tilting experiments, [ref. Fig. 2], it was possible to elucidate its structure as hcp. Note that this oxide is paramagnetic at room temperature[9] and could act as nucleation sites for reverse domains. This would explain the low coercivity in these samples.

CONCLUSIONS : The good magnetic properties of this system is due to the tetragonal $RE_2Fe_{14}B$ phase, which has a large magnetocrystalline anisotropy. The reason for the high coercivity is thought to be due to the presence of continuous films of the non-magnetic grain boundary fcc phase, enriched in Ce, Pr and Nd. In samples with poor coercivity, a large concentration of the rare-earth sesqui-oxide has been observed. The main reasons for the increase in coercivity on annealing at 600°C are : (1) the annealing of defects at the grain boundaries, which act as nucleation centers for reverse domains ; (2) the formation of more continuous films of the non-magnetic grain boundary phase, which magnetically isolates each magnetic tetragonal grain. Further investigation is in progress to study this mechanism.

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FIGURE CAPTIONS

Figure 1 : Bright field micrograph of the grain boundary phase in the <100> zone axis orientation. Insets show the EDX spectra of the fcc phase and the matrix as well as the [001] zone axis SAD pattern of the matrix.

Figure 2 : A tableau of Microdiffraction patterns from the grain boundary phase showing the <100>, <110>, <111>, <112>, <114> zone axis patterns and thus confirming an fcc structure.

Figure 3 : Bright field micrograph of the sesquioxide of the rare earths in the <0001> orientation along with the EDX spectra, which is also compared to that of the matrix phase.

TABLE I

REGION	ELEMENT & LINE	WEIGHT PERCENT	ATOMIC PERCENT	INTENSITIES [ARB.]
TETRAGONAL PHASE	Fe K	70.11	85.76	88.53
	Ce L	2.19	1.07	1.03
	Pr L	4.68	2.27	2.22
	Nd L	23.02	10.90	10.73
FCC PHASE [WITHOUT OXYGEN]	Fe K	12.29	26.39	14.06
	Ce L	12.28	10.51	5.26
	Pr L	20.55	17.48	8.82
	Nd L	54.88	45.61	23.19

REGION	ELEMENT & LINE	WEIGHT PERCENT	ATOMIC PERCENT	INTENSITIES [ARB.]
FCC PHASE [WITH OXYGEN]	O K	7.62	38.22	2.75
	Fe K	11.32	16.26	14.26
	Ce L	11.58	6.63	5.47
	Pr L	19.07	10.86	9.02
	Nd L	50.40	28.03	23.45
RARE EARTH SESQUIOXIDE	O K	27.85	76.33	8.13
	Fe K	3.38	2.65	3.45
	Ce L	3.29	1.03	1.26
	Pr L	12.70	3.95	4.86
	Nd L	52.71	16.05	19.86

THEORETICAL K-FACTORS

ELEMENT AND LINE	K-FACTORS	ELEMENT AND LINE	K-FACTORS
O K	1.2888	Pr L	0.9842
Fe K	0.3694	Nd L	1.0000
Ce L	0.9862		

* NOTE : In all the analyses, boron is not included as the boron x-rays are absorbed by the detector.

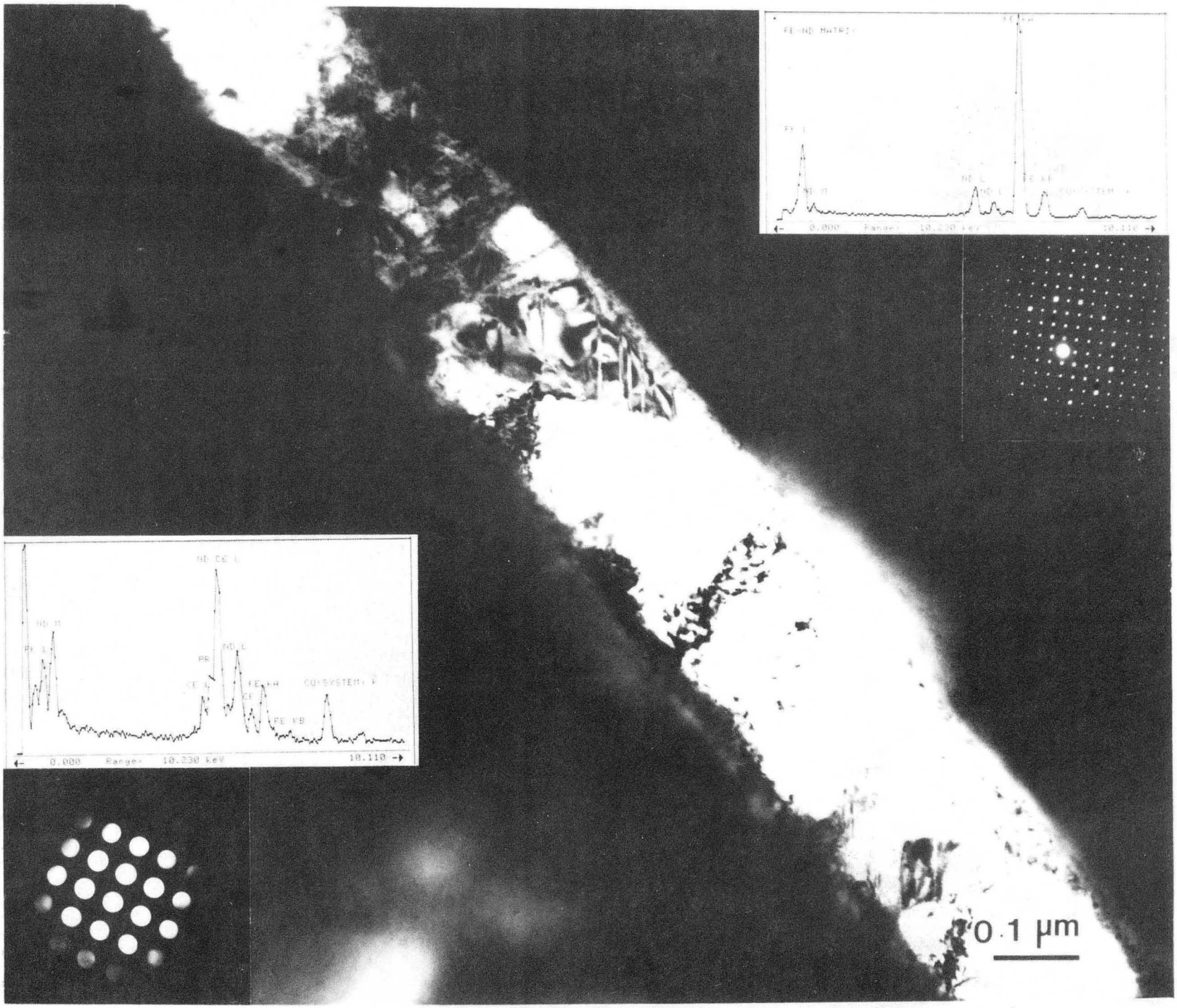

Fig. 1

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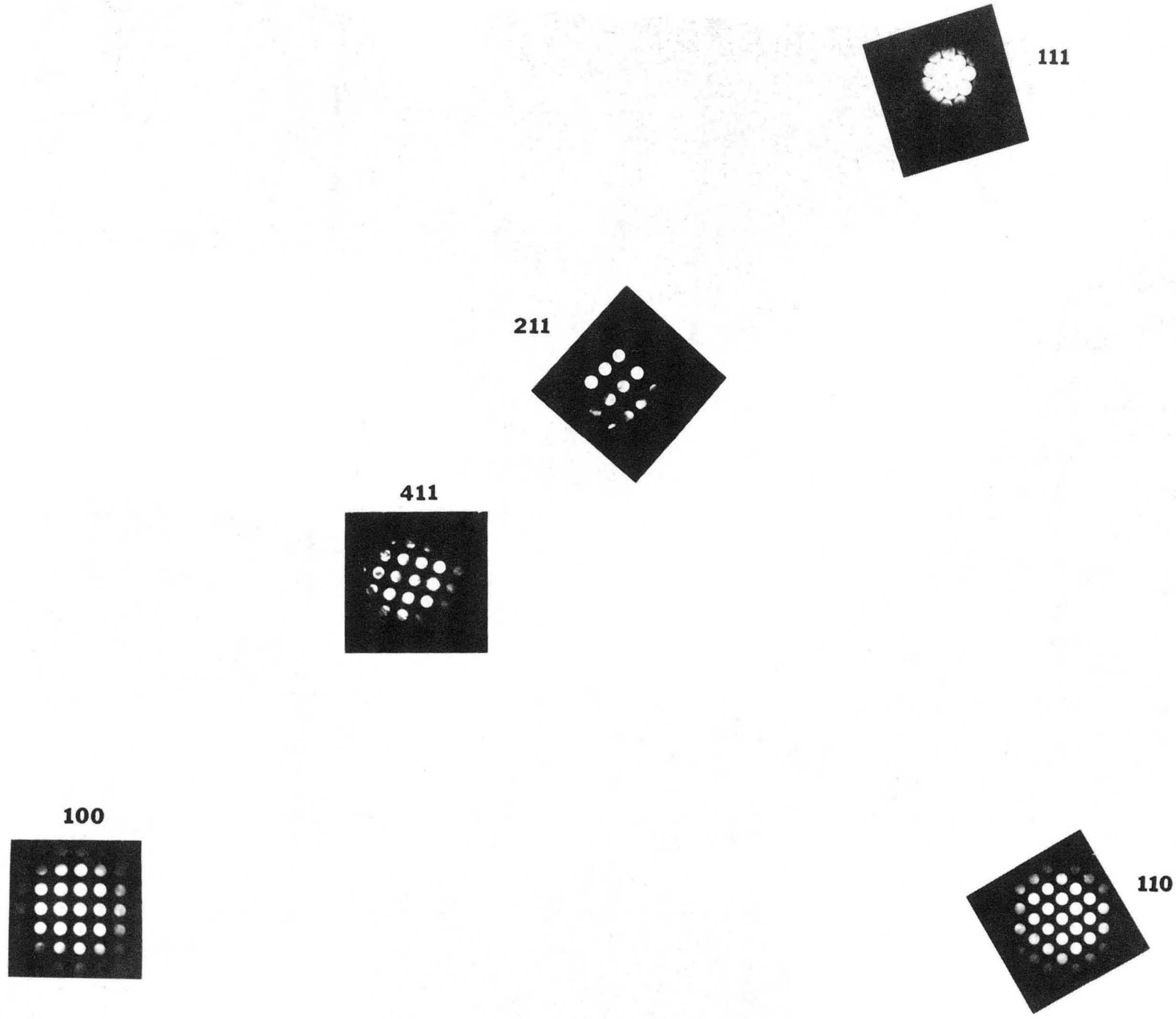

Fig. 2

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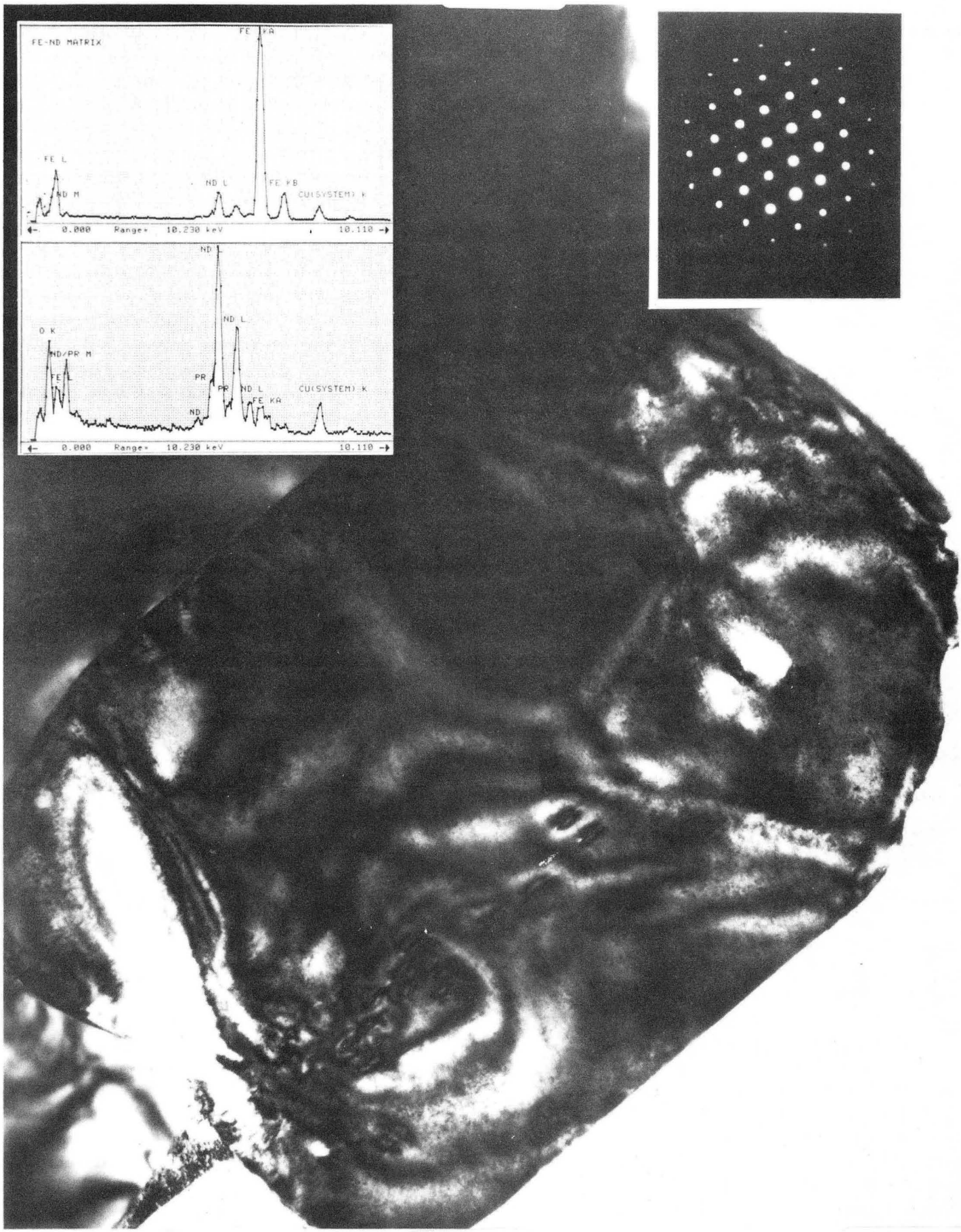

Fig. 3

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