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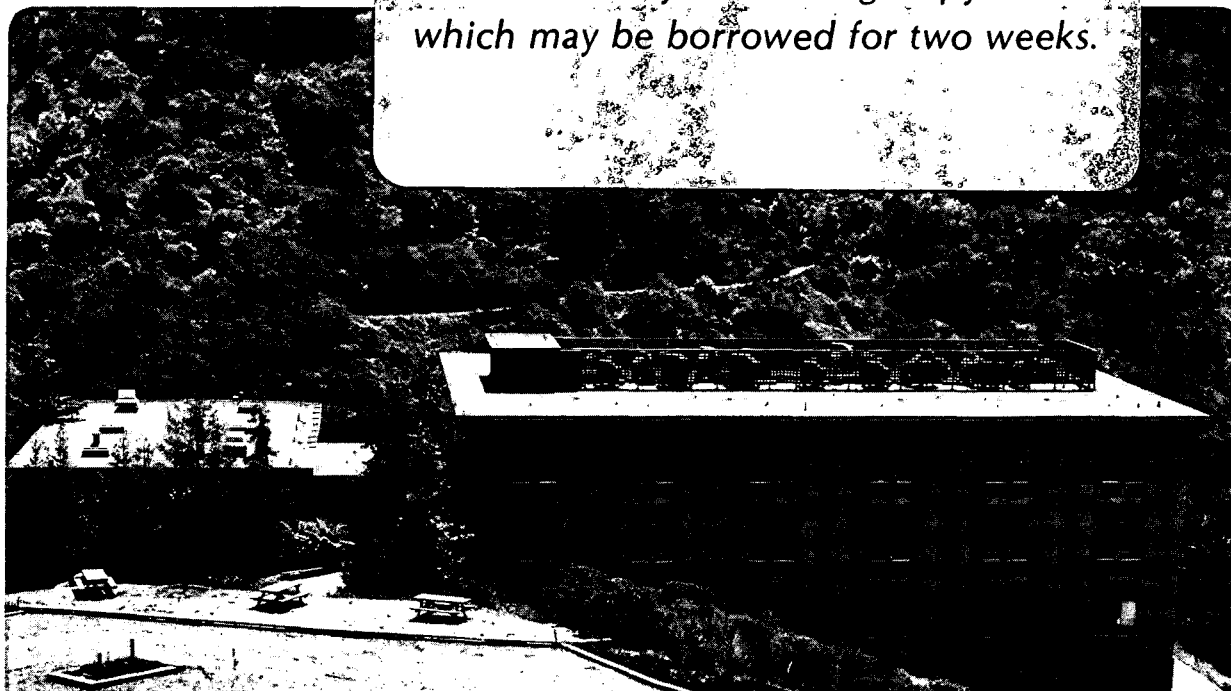
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EFFECT OF Dy ADDITIONS ON MICROSTRUCTURE AND MAGNETIC PROPERTIES OF Fe-Nd-B MAGNETS

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EFFECT OF Dy ADDITIONS ON MICROSTRUCTURE AND MAGNETIC PROPERTIES
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ABSTRACT :

This paper addresses the effect of Dy addition upon the magnetic properties, microstructure and microcomposition of Fe-Nd-B magnets. It is shown that increasing additions of Dy causes the remanence, B_r to decrease linearly. The intrinsic coercivity, iH_c , increases sharply for small additions of Dy, but the increase is not proportional for higher Dy contents. The iH_c increases almost linearly with the effective anisotropy field of the $RE_2Fe_{14}B$ phase until the Dy content is about 10% of the total rare earth content. Above this concentration, there is a strong deviation from linearity. Various types of possible concentration profiles of the substituted rare earth are suggested. It is also argued that preferential segregation of Dy to the interfaces could be beneficial in increasing the nucleation field. Morphologically there is no apparent effect of Dy on the microstructure. However, in the 5 atomic % Dy sample, Dy rich oxides were observed. It is shown through Energy Dispersive Xray Spectroscopy (EDXS) line profiling that Dy partitions preferentially into the $RE_2Fe_{14}B$ phase in all the cases. No segregation of Dy to the interphase interfaces has been detected.

INTRODUCTION :

Current industrial and academic interest in Fe-Rare Earth-B permanent magnets is well evidenced by the number of conference symposia and workshops being held on this class of magnets. Since the discovery of these magnets[1-3], considerable advances have been made in the understanding of their structure, microstructure and properties [4,5], although some questions still remain regarding the actual site for initiation of magnetization reversal. One of the efforts now is in improving the temperature dependent properties through alloying additions. These efforts are being made to offset the high temperature coefficient of iH_C and B_r , due to the low Curie temperature, T_C , of the $RE_2Fe_{14}B$ phase. Thus, Dy, Tb, Al additions have led to significant improvements in the intrinsic coercivity, while Co addition has helped in raising the Curie temperature of the $RE_2Fe_{14}B$ phase[6-12]. It has also been shown that addition of small amounts of Zr can still improve the anisotropy field[13]. However, heavy rare earths such as Dy or Tb decrease the magnetization due to the ferrimagnetic coupling between the rare earth atom and the Fe atoms. Thus, the effect of these additions in the case of single crystal samples, on the magnetic properties are well understood. Recently, Hirose et al[14] have examined the relationship between iH_C and H_A of heavy rare earth (Dy and Tb) substituted Fe-RE-B magnets and also the influence of temperature and concentration of heavy rare earth on iH_C and H_A .

In the case of sintered magnets, however, the effects may be more complex due to the polycrystalline nature as well as due to microstructural influences. Thus, the addition of a quaternary element, such as Dy, can bring about two possible changes:(1) a change in the intrinsic properties (such as H_A, M_S) of the 2-14-1 phase with no change in the microstructure and composition;(2) a change in the microstructure (such as the appearance of a new phase) and/or microcomposition of the magnet. Both these potential changes will influence the iH_C , B_r and $(BH)_{max}$ of the magnet. Thus, a systematic study of the influence of these additions on the magnetic properties, microstructure and microcomposition is essential. The microstructure and magnetic properties are sensitive to changes in alloy composition and processing conditions. Thus it is also important to study the effect of each element independent of the influence of other such additions. Hence, controlled samples have to be made and their properties measured and microstructure

characterized.

The distribution of the substituted rare earth in the microstructure will depend upon the processing conditions adopted. Figs.1a(i-iv) show schematically a few of the possible concentration profiles for the quaternary element. In this case, a microstructure similar to that observed in the case of sintered Fe-RE-B magnets is examined. The microstructure, shown in Fig.1b, consists of grains of the $\text{RE}_2\text{Fe}_{14}\text{B}$ phase, at the junctions of which exists a RE rich fcc phase which often extends through the two-grain boundaries[19]. Fig 1a(i) is a case where there is no partitioning of the additive to the grain boundary phase or the 2-14-1 phase. In (ii) the additive element partitions preferentially into the 2-14-1 phase while the converse is the case for (iii). In (iv) is shown a concentration profile wherein the additive segregates to the interface between the two phases. This type of segregation could also occur at grain boundaries. In all the cases, the arrows indicate the interface between the matrix and the grain boundary fcc phase. Among all these hypothetical concentration profiles, (iv) is most interesting, if it is practically achieved in the case of a substitutional element such as Dy. $\text{Dy}_2\text{Fe}_{14}\text{B}$ has a very high anisotropy field (158 kOe) as compared to 71kOe for $\text{Nd}_2\text{Fe}_{14}\text{B}$ [15-17]. In such a case, it would be possible to obtain a very localized increase in the magnetocrystalline anisotropy (and hence a high local anisotropy constant), thus increasing the nucleation field required to nucleate a reverse domain wall at the grain boundary or two-phase interface. Such interfaces are generally accepted to be the sites of domain wall nucleation in this class of magnets. Note that this does not appreciably alter the bulk magnetization of the matrix $\text{RE}_2\text{Fe}_{14}\text{B}$ phase, as is the case when the heavy rare earth element is homogeneously distributed in the matrix. Thus, it is clear that by altering the microstructure and/or the composition close to the grain boundaries (or two phase interfaces), considerable changes in the magnetic properties could be potentially brought about.

With this in mind, a systematic investigation of the microstructure and magnetic properties of substituted Fe-Nd-B sintered magnets was initiated. The quaternary addition was systematically varied, keeping the total rare earth content constant. The influence of such changes upon the magnetic properties was correlated with the microstructure and microanalysis of the magnets. Here the results of the Dy addition are reported.

EXPERIMENTAL PROCEDURES:

(1) Alloys : The alloys were prepared by vacuum induction melting and processed into aligned magnets by traditional Powder Metallurgy(P/M) technique[18]. Magnets were sintered in the temperature range of 1000°C and 1100°C for three hours and then cooled to room temperature. An isothermal treatment in the temperature range of 500°C to 700°C for three hours was then applied to obtain the optimum intrinsic coercivity (iH_c).

(2) Magnetic Measurements: All magnets were magnetized in a pulsed magnetic field of 35kOe prior to each measurement. Magnetic properties were measured using a Hysteresigraph at a maximum applied field of 25kOe.

(3) Transmission Electron Microscopy and Analytical Electron Microscopy: Electron transparent thin foils were made by Argon ion -milling discs which had been mechanically thinned down to a thickness of about 50 micrometers. In some cases, the sample was dimpled to reduce the milling time. Argon ion-milling was carried out at 6kV with a gun current of 0.3 mA, corresponding to a specimen current of 20-30microamperes. The milling was completed in about 12-15 hours.

Transmission Electron Microscopy(TEM) imaging was carried out using a Philips 400 TEM/STEM at 100kV. Analytical electron microscopy was carried out using a JEOL 200CX microscope at 200kV. This microscope is fitted with an ultra-thin window Energy Dispersive Xray(EDX) detector as well as a regular Be window EDX detector. The use of the ultra-thin window detector enables the detection and quantification of light elements such as oxygen. Spectral deconvolution and quantification was carried out on the KEVEX 8000 system software using theoretically generated thin foil k-factors. Care was taken to ensure statistical significance of the data by acquiring a minimum of 10⁵ counts. Microanalysis line profiles were carried out at different regions in order to check the correctness of the profiles as well as the reliability of the data.

RESULTS AND DISCUSSION:

(1) Magnetic Properties : The addition of increasing amounts of Dy causes

the remanence, B_r , to decrease progressively, as is shown in Fig.2. The trend exhibited can be explained as due to the ferrimagnetic coupling between the Fe spins and the Dy spins. As the Dy content of the alloy is increased, the Dy content of the $RE_2Fe_{14}B$ phase also increases (see section on Microstructure and Microanalysis) and hence the remanence drops. The intrinsic coercivity, iH_c , on the other hand, shows a sharp rise for small additions of Dy. However, above about 10%Dy (i.e., corresponding to $Nd_{0.9}Dy_{0.1}Fe_{14}B$) the rate of increase in iH_c drops, Fig.3. Since both the iH_c as well as the anisotropy field increase with increasing additions of Dy, a correlation between iH_c and the anisotropy field can be expected. In an earlier paper, Hirosawa et. al have shown that the iH_c increases linearly with anisotropy field for values of the anisotropy field in the range 70-80 kOe. In this investigation, a larger range of Dy content has been examined. In Fig.4 the iH_c is plotted against the effective anisotropy field. The effective anisotropy field is calculated as follows :

$$\text{Effective Anisotropy Field } (H_A \text{ eff.}) = X_{Nd} \cdot H_A^{Nd} + X_{Dy} \cdot H_A^{Dy},$$

where X_{Nd} is the relative atomic fraction of Nd and X_{Dy} is the relative atomic fraction of Dy ; H_A^{Nd} and H_A^{Dy} are the anisotropy fields of $Nd_2Fe_{14}B$ and $Dy_2Fe_{14}B$ respectively. The assumption here is that the $RE_2Fe_{14}B$ phase is made up of a homogeneous mixture of $Nd_2Fe_{14}B$ and $Dy_2Fe_{14}B$ with the fractions X_{Nd} and X_{Dy} respectively. In the initial portion of the curve (i.e., for low Dy contents) the dependence is linear, as was observed by Hirosawa et. al. However, at higher concentrations, the slope of the curve drops. This indicates that for higher Dy concentrations, some changes in the microstructure may be occurring, which may be limiting the achievement of a higher value of iH_c .

MICROSTRUCTURE AND MICROANALYSIS :

In an earlier paper, the microstructure of Nd-Fe-B magnets has been discussed in detail[19]. It was shown that the grain boundary phase is fcc and is stabilized by significant quantities of oxygen. The overall microstructure (morphology) was the same for all the magnets examined in this investigation and is described in [19]. Hence, microanalytical characterization was carried out with two main objectives : (1) to examine the partitioning of Dy between the grain boundary phase and the matrix, or segregation of Dy to the grain boundaries or two phase interfaces ; (2) to examine whether Dy rich second phase particles appear

for the highest Dy concentration sample, which shows a marked deviation from linearity. Note that since these measurements are made at room temperature only, a linear relationship between iH_c and the anisotropy field can be expected. Hence, x-ray microanalysis was carried out on the two samples marked A and B in Fig.3, to see whether there was any difference in the microanalytical details at high Dy concentrations.

The distribution of Dy in the microstructure was examined by line profiling, which is shown schematically in Fig.5. In this case, line profiling has been carried out across the triple grain junction. Fig.6(a) shows a typical profile in sample A, which is the high Dy sample. The plot indicates that Dy partitions preferentially to the matrix phase, as shown more clearly in Fig.6(b). As can be seen from Fig.6(b), within the experimental limits of EDXS analysis there is no significant partitioning of Dy to the grain boundary phase, although one might expect Dy, as with the other rare earth elements, to be associated with the oxygen stabilized grain boundary phase[19]. On the contrary, the trends indicate that Dy is preferentially segregated away from the grain boundary phase and the interfaces. This means that the increase in iH_c observed is mainly due to the increase in the Dy content of the matrix phase. However, in sample A the Dy concentration of the matrix (3.7-4.0 at.%) was consistently and repeatably found to be less than the nominal Dy content of the alloy, i.e., 5 at.%. This indicated that some of the Dy could exist as inclusions, oxides, etc. Examination of the microstructure of sample A did reveal the presence of such inclusions. One such example is shown in Fig.7(a), while Fig.7(b) shows the corresponding EDX spectrum from this particle. Quantification yielded a composition of 59 at.% Nd and 41 at.% Dy. Since this spectrum was obtained with a Be window detector, the possible presence of oxygen is not revealed. However, it is quite possible that it is an oxide phase. The presence of such Dy-rich inclusions justifies the drop in iH_c observed for sample A (see Figs. 3 and 4), since it not only reduces the Dy content of the matrix phase (thereby reducing the effective anisotropy field), but also provides potential sites for the nucleation of reverse domains. Fig. 8(a) shows the composition profile for alloy B, which is the lower Dy content sample. In this case Dy partitions completely into the matrix and the grain boundary phase does not contain any detectable amount of Dy, as seen from Fig.8(b). Thus if Dy is added at the induction melting stage, as in this case, it partitions almost completely into the matrix (corresponding to case (ii) in Fig.1(a)). Thus a Dy concentration profile, such as that shown in Fig.1(a)(iv), may not be possible to achieve by the processing technique adopted in the preparation

of the magnets examined in this study. However, it is possible that such a concentration profile can be achieved by the addition of: (i) pure Dy metal before the sintering stage such that Dy diffuses along grain boundaries and interfaces and into the matrix during sintering; (ii) a compound of Dy such as Dy_2O_3 , which could react with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, displacing Nd with the resulting enrichment of Dy in the matrix phase.

The first method has the drawback that Dy has a higher melting point (1412°C) than the sintering temperatures generally employed. The second method has been adopted by Ghandehari[20] to produce magnets with high $i\text{H}_c$ (comparable to that of Dy-substituted magnets). However this method also has the drawback that the presence of the oxide causes a decrease in the remanence and possibly provides easy nucleation sites for the nucleation of domain walls.

CONCLUSIONS :

The effect of Dy addition upon the magnetic properties, microstructure and microcomposition of Fe-Nd-B magnets has been investigated. It has been shown that there is a linear decrease in the remanence of the magnet with increasing Dy addition. The intrinsic coercivity, on the other hand, increases sharply for small additions of Dy. Additions of Dy above 10% of the total rare earth content does not produce a concomitant increase in the $i\text{H}_c$. The intrinsic coercivity increases linearly with the effective anisotropy field for Dy contents upto about 10% of the total rare earth content. Above this concentration, there is a sharp deviation from linearity. This is attributed to the incomplete ingestion of Dy into the $\text{RE}_2\text{Fe}_{14}\text{B}$ phase leading to the formation of other Dy-rich phases. Various types of possible concentration profiles of the substituted rare earth element have been suggested. In all the cases studied experimentally, it appears from the EDXS analyses (within the limits of experimental error) that Dy partitions preferentially into the matrix phase. No segregation of Dy to the interphase interfaces has been detected by EDXS. It is suggested that in order to preferentially segregate Dy to the interphase interfaces, non-conventional processing techniques such as addition of Dy_2O_3 or low melting Dy-rich alloys be examined. In this way, it may be possible to increase the anisotropy constant locally, near the grain boundaries and two phase interfaces.

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FIGURE CAPTIONS

Figure 1(a) (i-iv): Schematic illustrations of various types of concentration profiles for the substituted rare earth element. (See text for description of each plot.)

Figure 1(b) : Transmission electron micrograph of the typical microstructure of the sintered magnet consisting of the matrix $\text{RE}_2\text{Fe}_{14}\text{B}$ phase at the junctions of which a rare earth rich oxygen stabilized phase exists and frequently extends into the two-grain boundaries.

Figure 2 : Effect of Dy content on the Remanence, B_r of Fe-Nd-B sintered magnet. The total rare earth content in all the cases is 35.1 wt.%.

Figure 3 : Effect of Dy content on the Intrinsic Coercivity, iH_c , of Fe-Nd-B sintered magnet. The total rare earth content in all the cases is 35.1 wt.%.

Figure 4 : Dependence of Intrinsic Coercivity upon the effective Anisotropy Constant, $e_{\text{eff}}H_A$. The total rare earth content is constant at 35.1 wt.%.

Figure 5 : Schematic illustration of the line profiling method across the interface of the $\text{RE}_2\text{Fe}_{14}\text{B}$ phase- grain boundary phase . The diameter of the spot corresponds approximately to the probe size.

Figure 6(a) : A typical elemental concentration profile in the case of Sample A (high Dy content); (b) An enlarged view of the Dy concentration profile. (The precision in quantification (2 sigma values) is within the width of the symbols).

Figure 7(a) : Bright field transmission electron micrograph of an inclusion in sample A ; (b) EDX spectrum from the inclusion in (a) , indicating that the inclusion is Dy-rich.

Figure 8(a) : A typical elemental concentration profile for the case of Sample B (low Dy content) ; (b) An enlarged view of the Dy concentration profile. (The precision in quantification (2 sigma values) is within the width of the symbols).

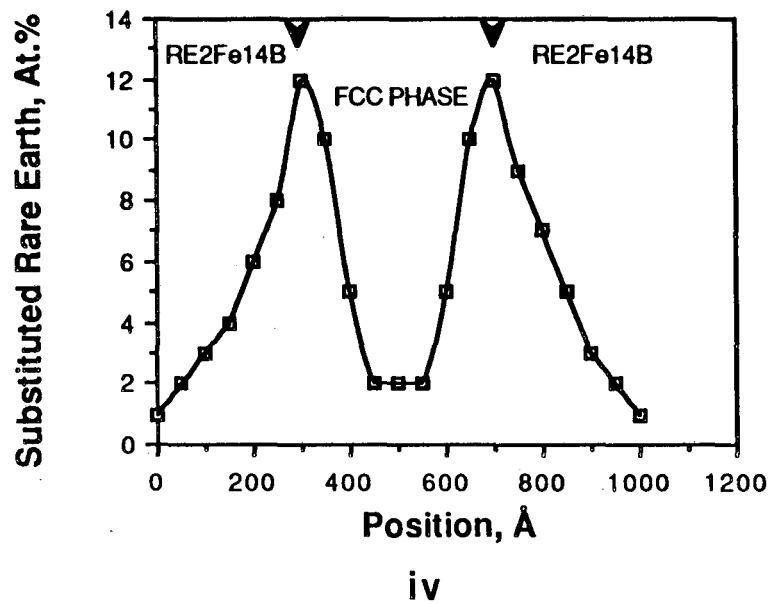
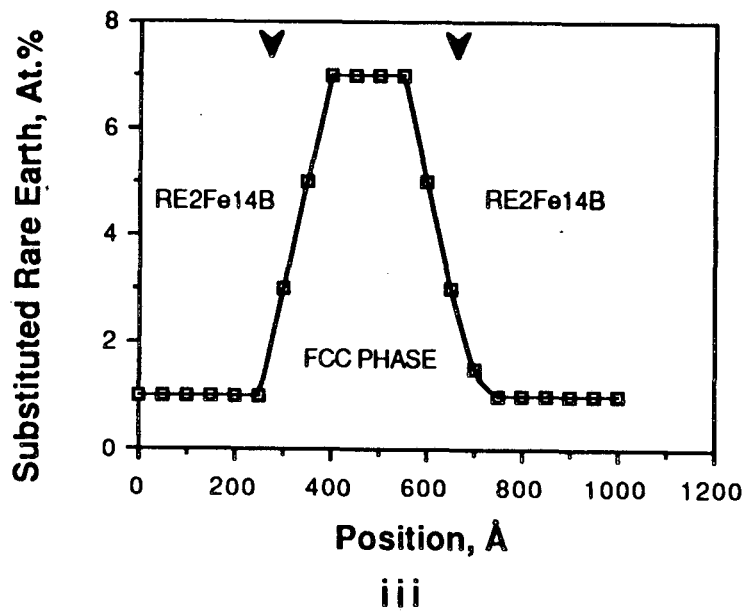
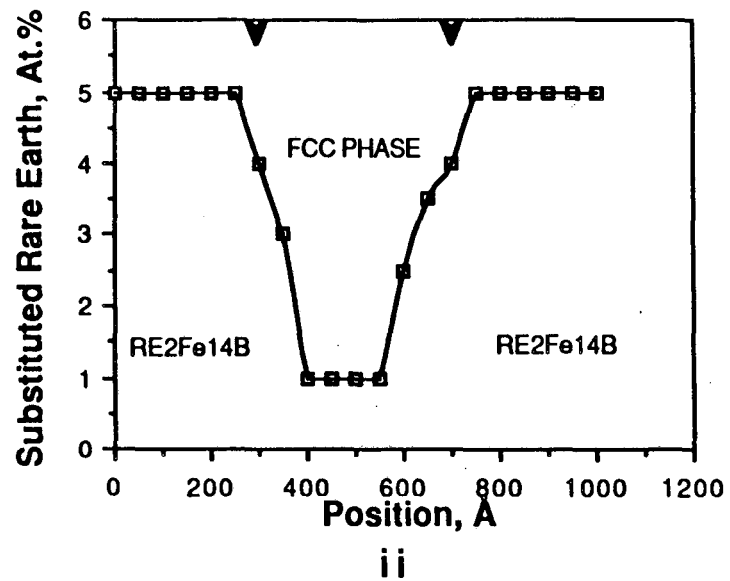
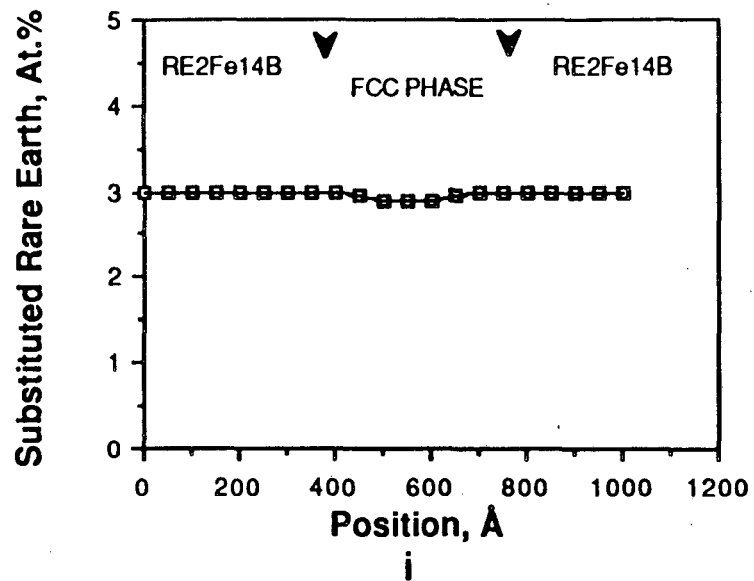
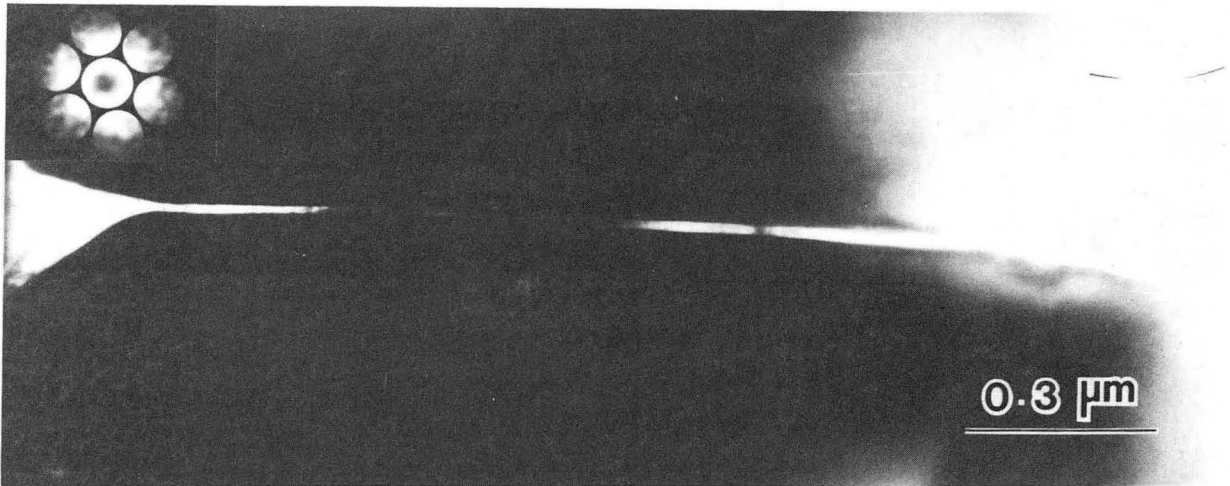


Fig.1 a



XBB 865-3633

Fig.1 b

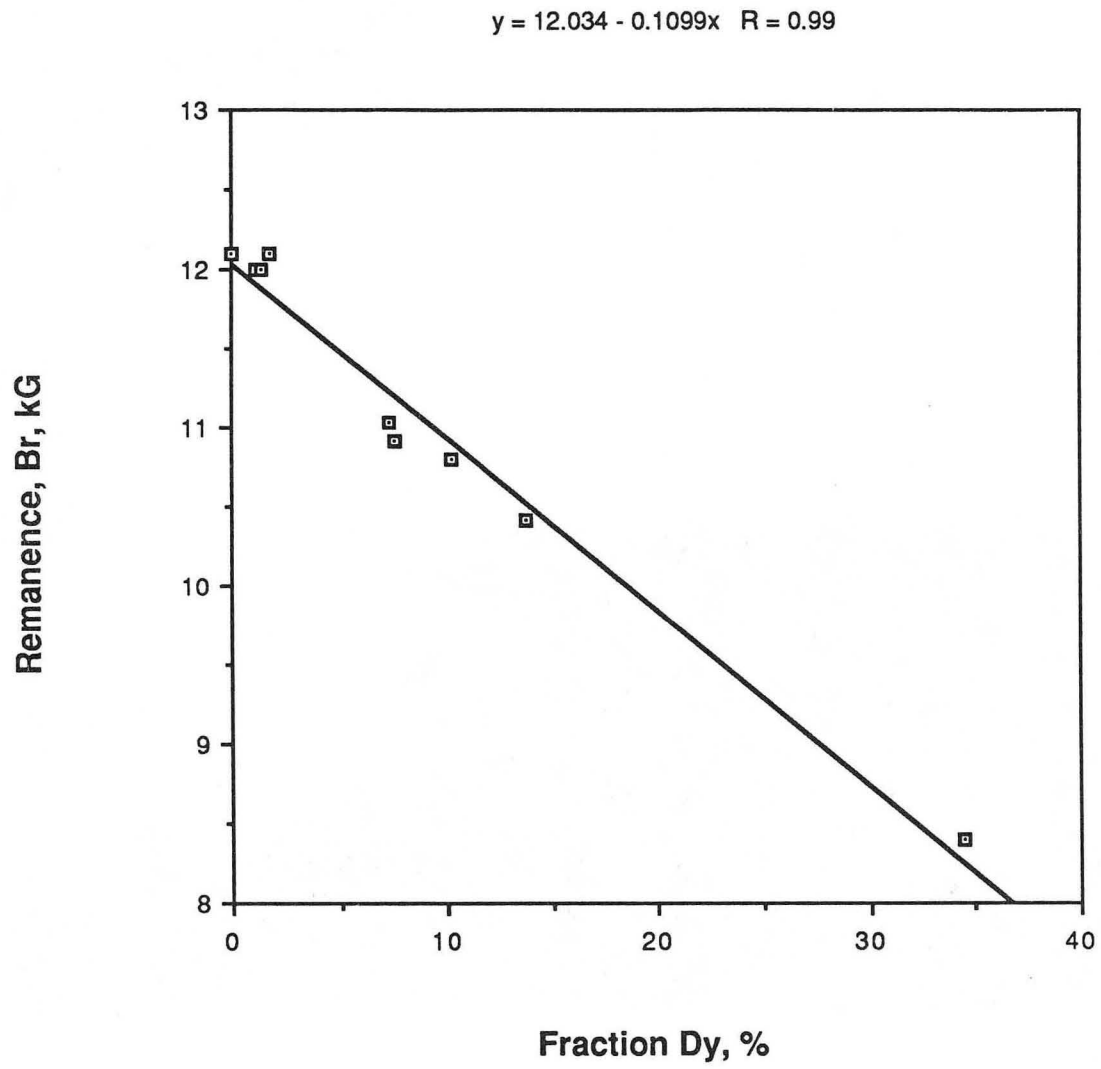


Fig.2

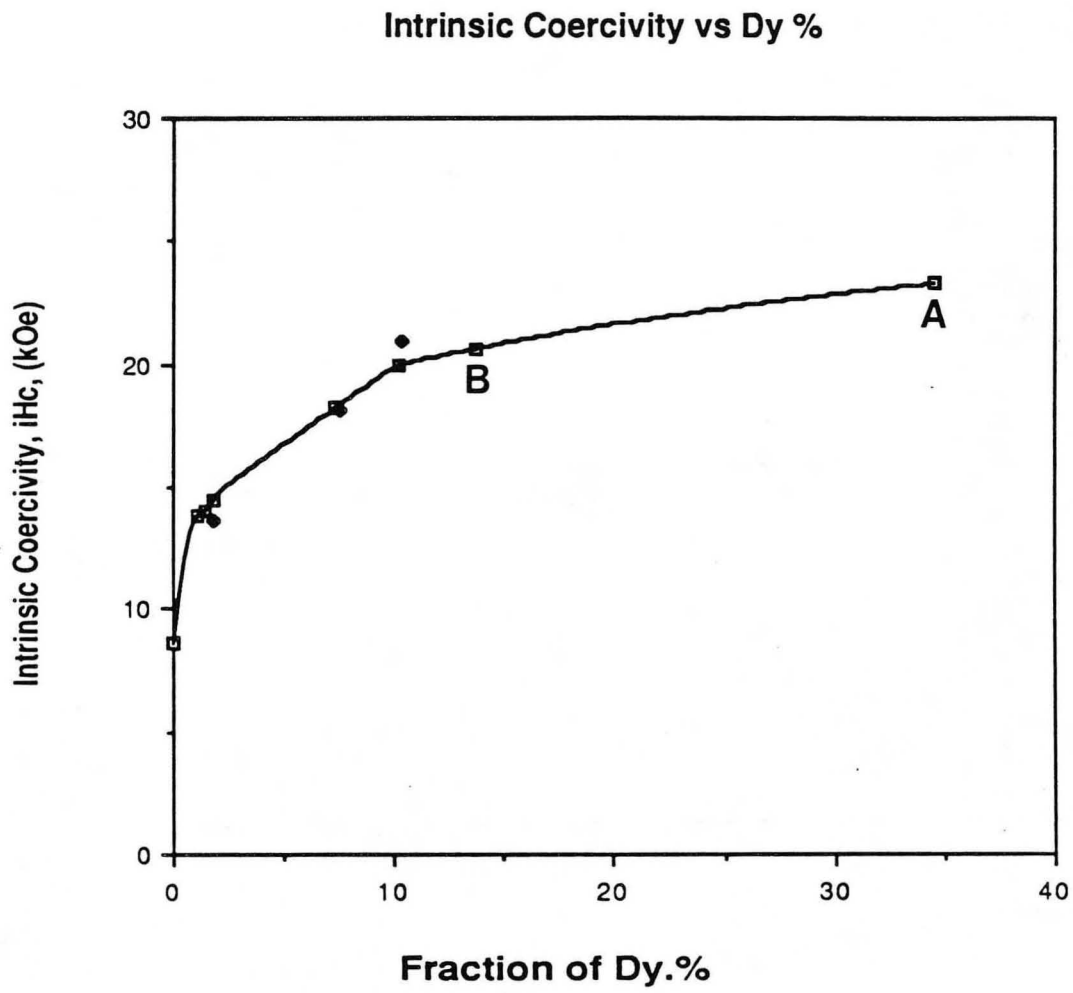


Fig.3

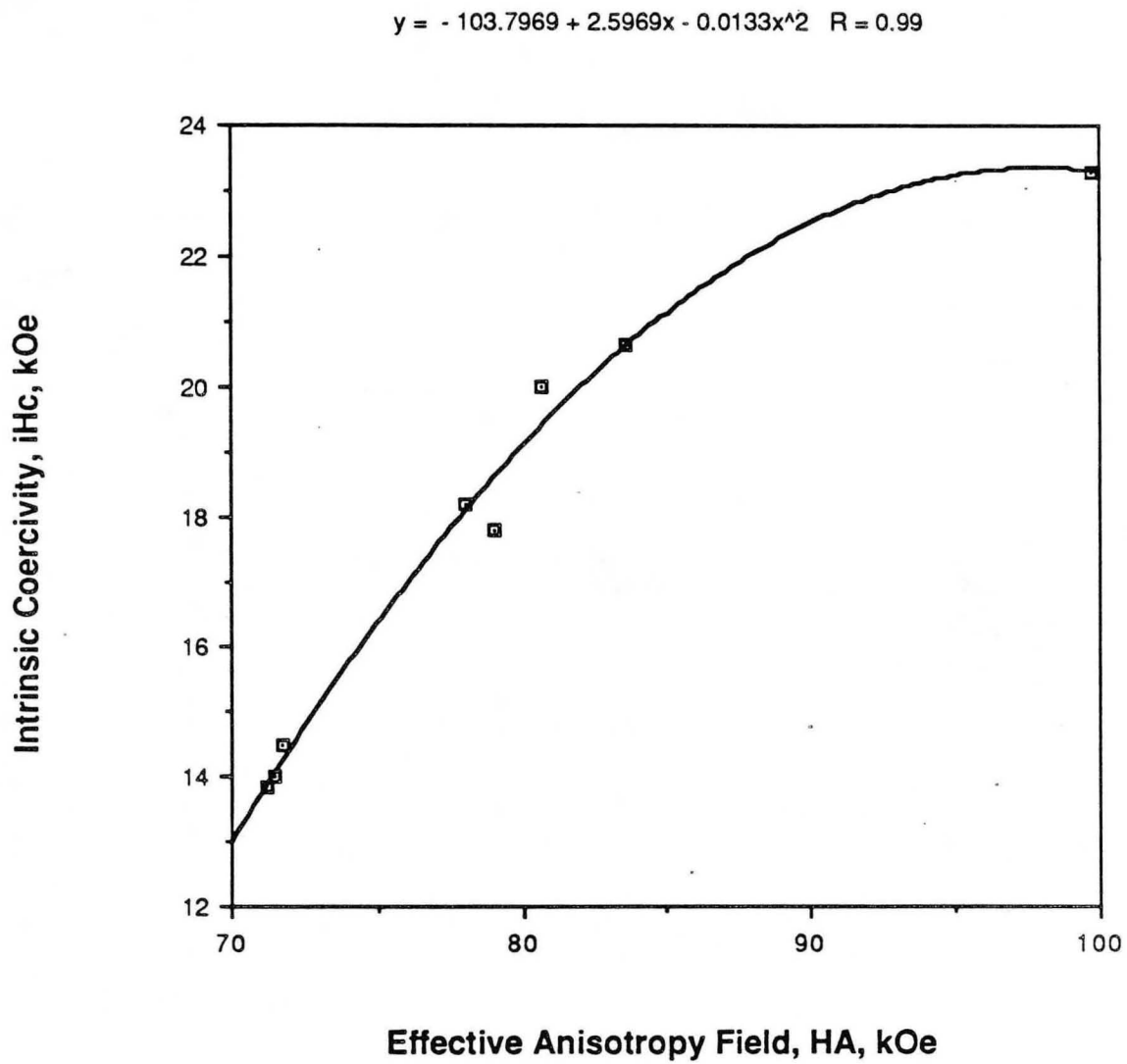
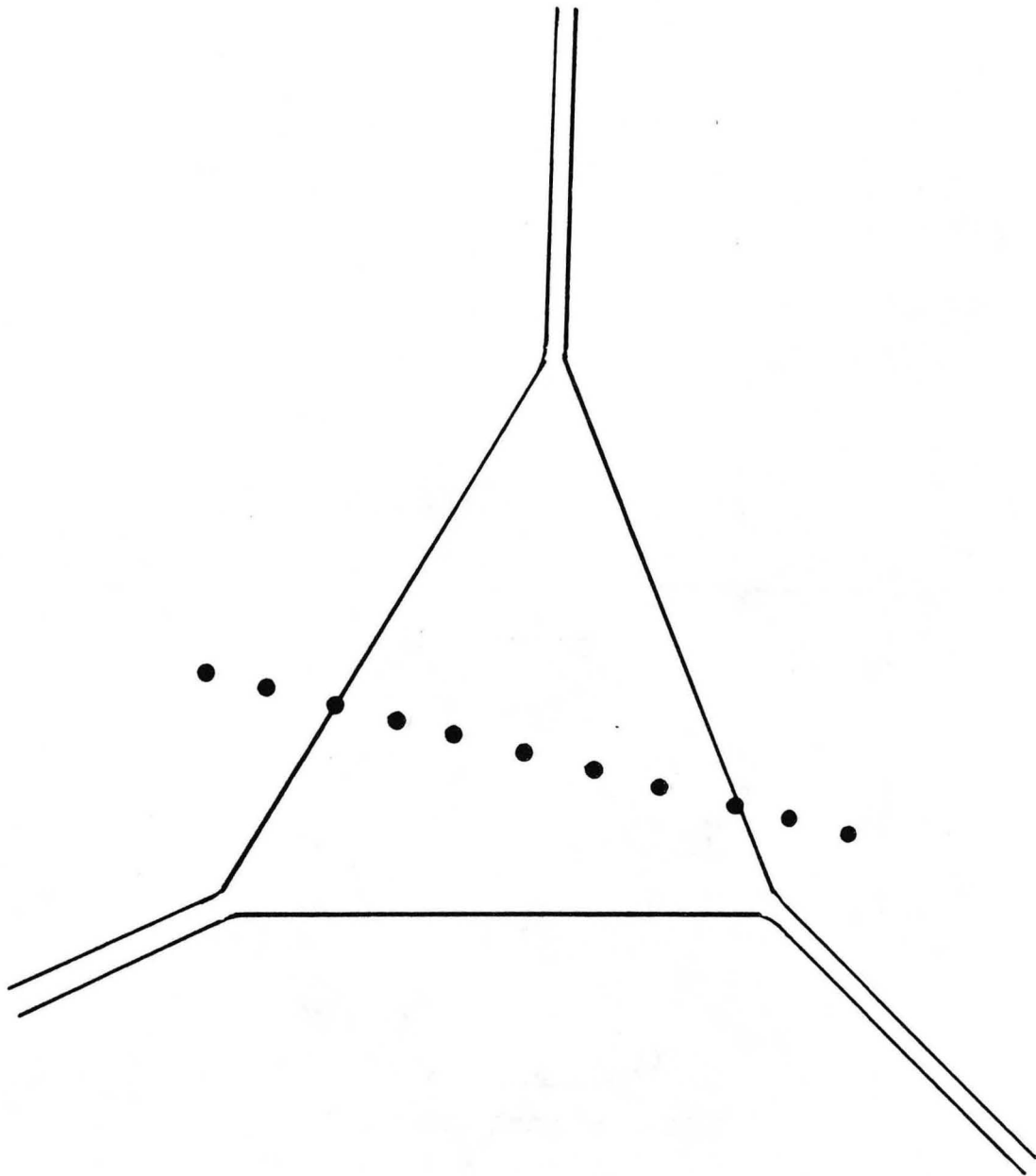


Fig.4



0.5 μm

XBL 868-2980

Fig.5

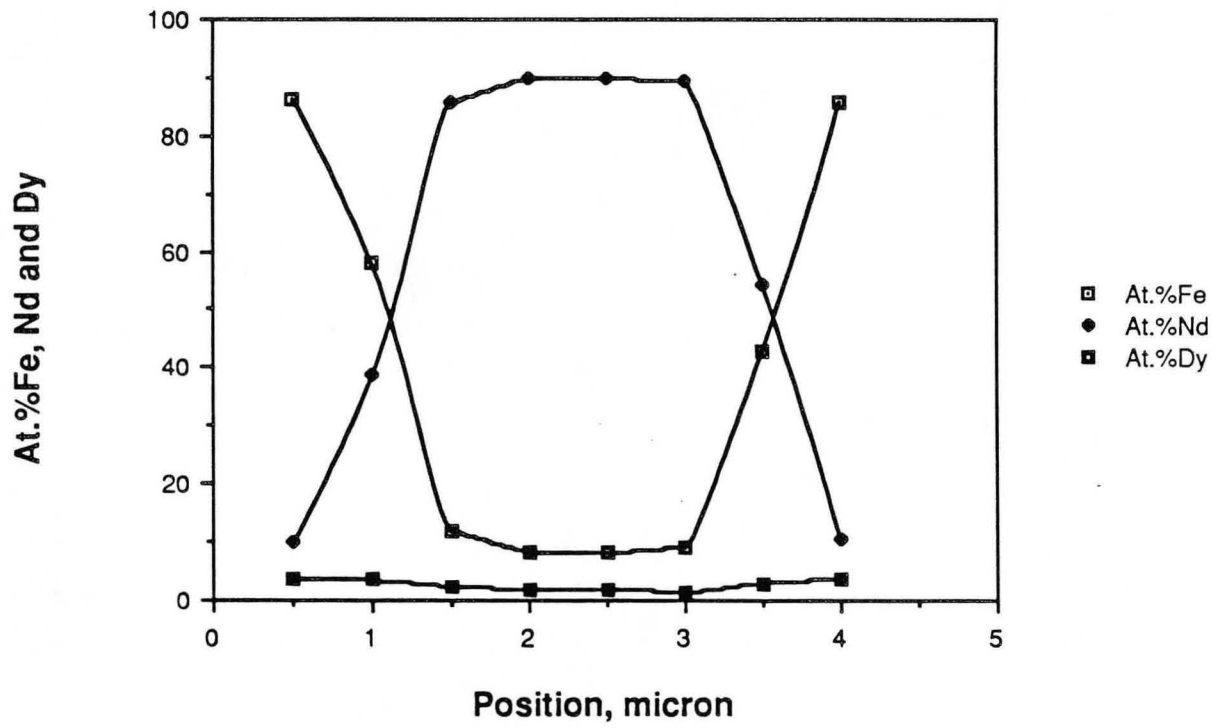


Fig. 6 a

Nominal Probe Size = 200Å

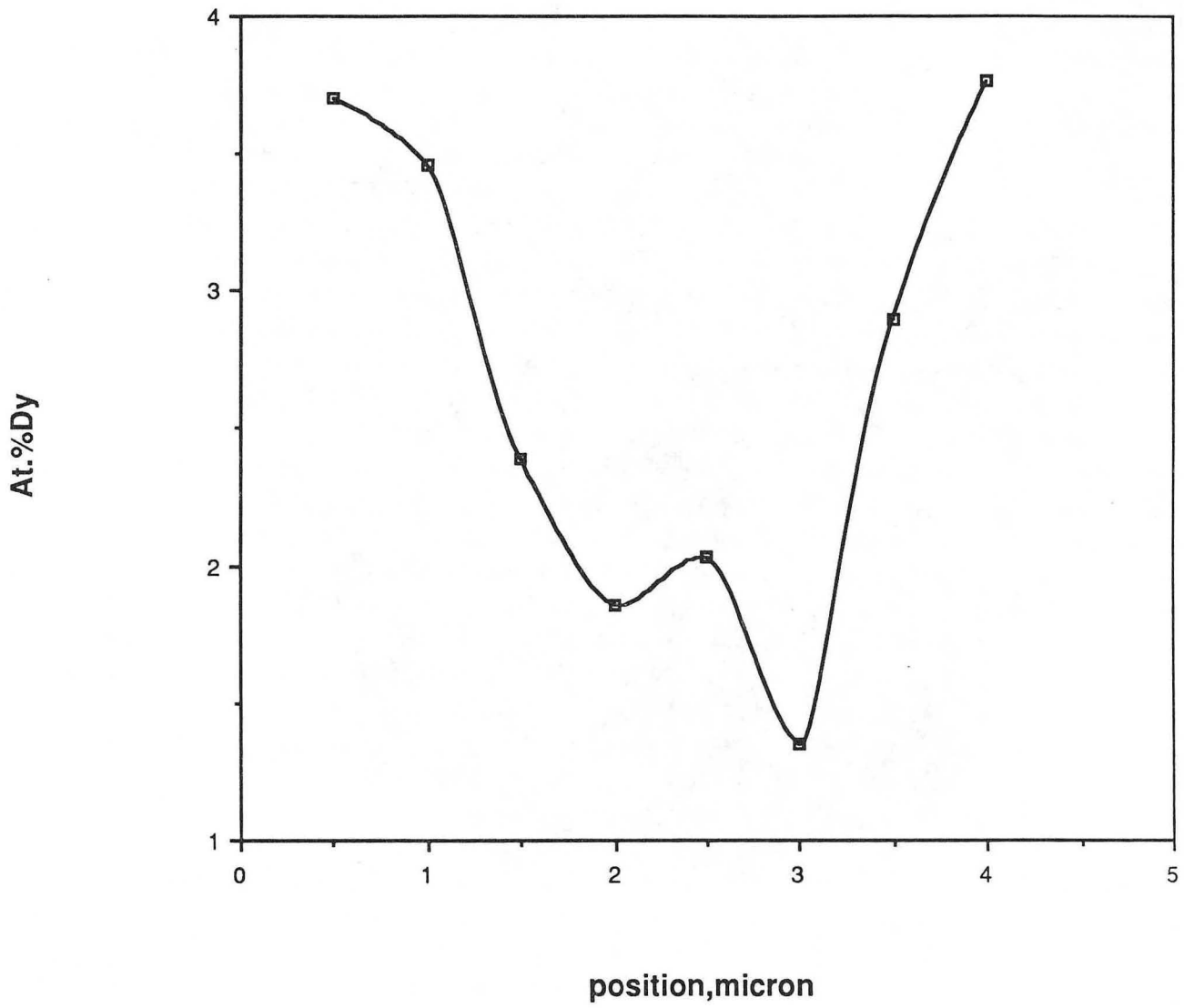


Fig. 6 b

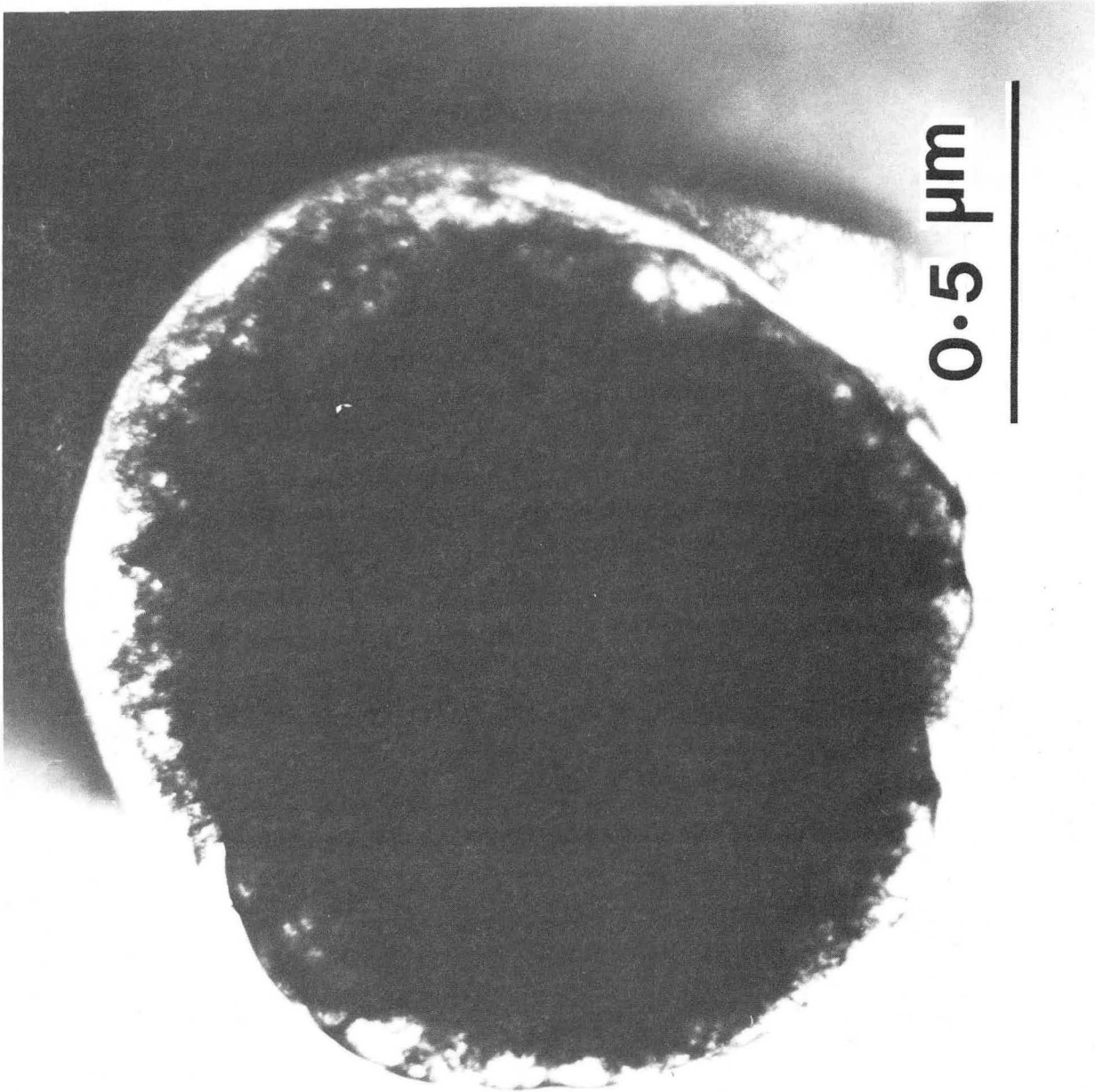


Fig 7a

XBB 874-2616

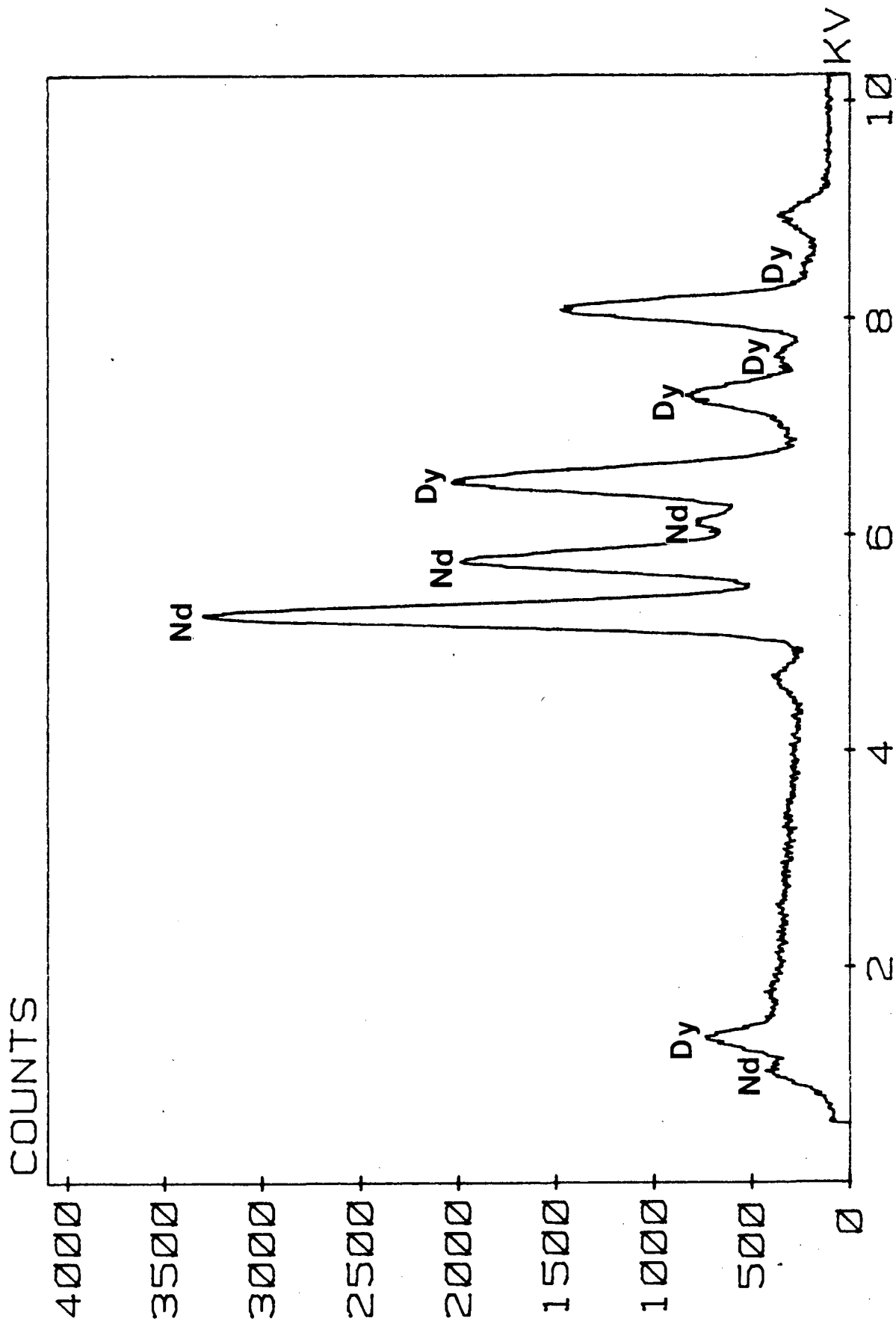


Fig 7 b

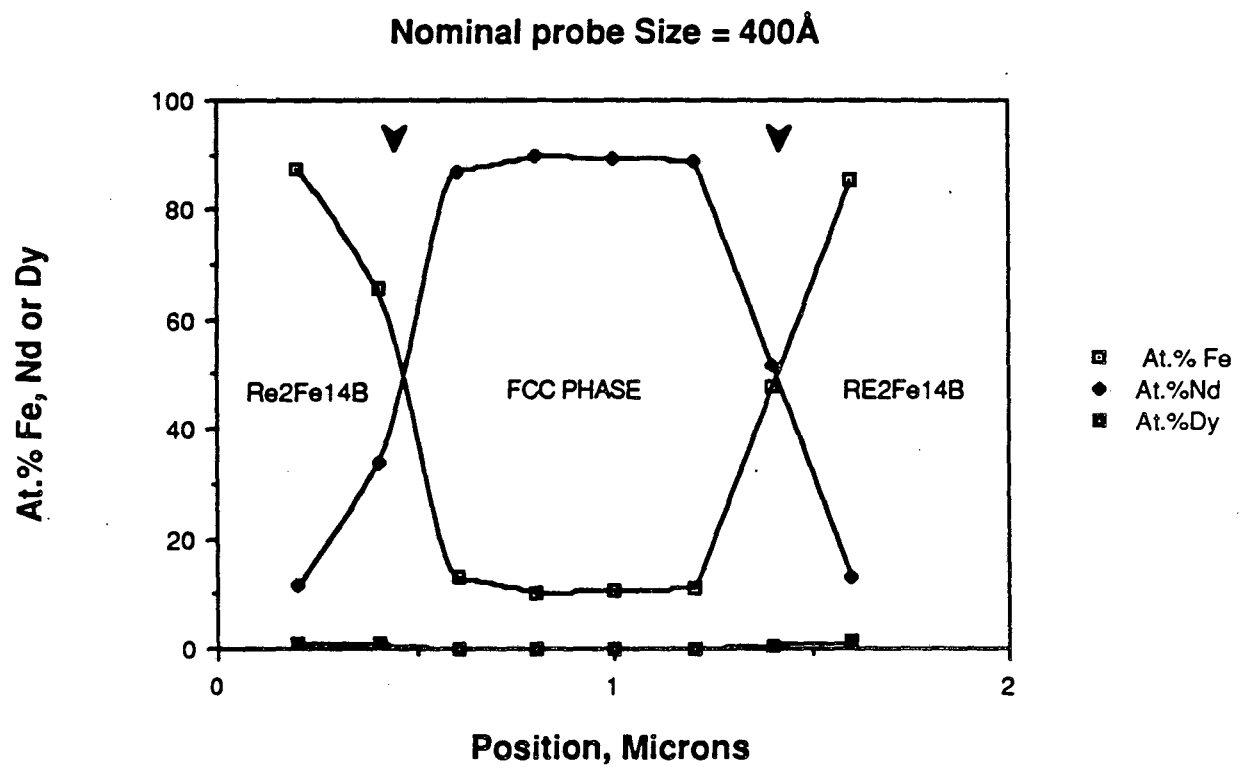


Fig. 8 a

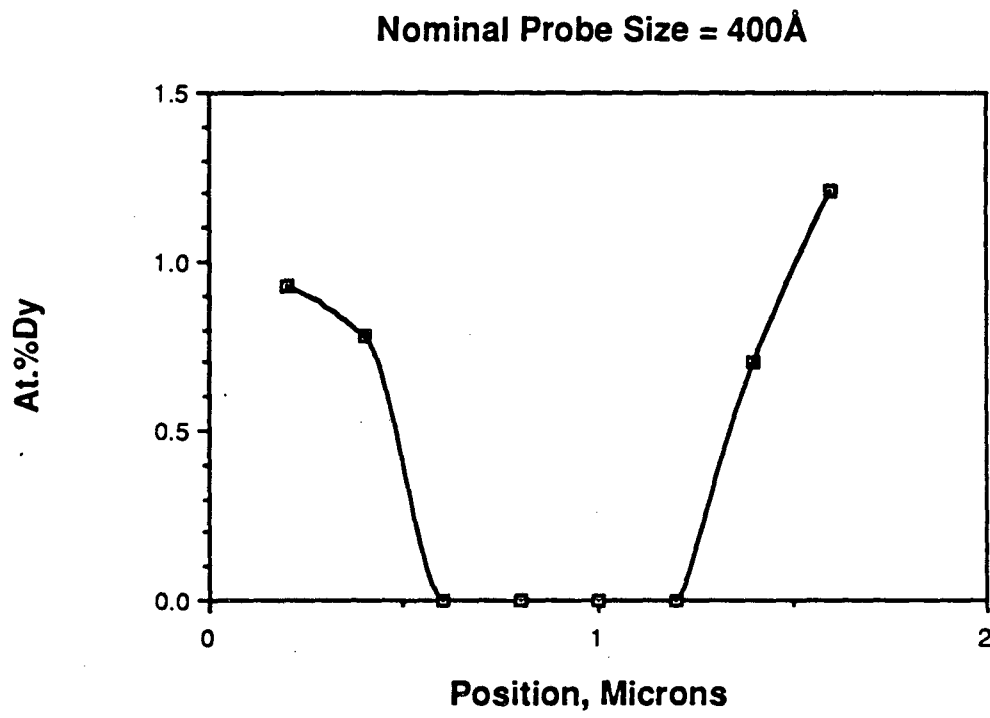


Fig. 8b

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