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SOME APPLICATIONS OF MICROANALYTICAL ELECTRON MICROSCOPY IN MATERIALS RESEARCH*

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Electron microscopy has made extraordinary progress over the past 30 years and has become an indispensable tool for research in materials science. In this paper a review is given of some applications of microdiffraction and microanalysis in our current materials science research projects at the University of California, Berkeley. The topics discussed include:

- a) The problem of solute atom partitioning in steels; this includes the difficulties of measuring carbon contents and methods of utilizing diffraction, lattice imaging, energy dispersive x-ray (EDXS) and electron energy loss (EELS) spectroscopies and atom probe analysis will be illustrated.
- b) Utilization of CBED and EDXS techniques in zirconia ceramics research.
- c) Applications of CBED to the study of γ -Fe₂O₃ particles used in magnetic recording systems.
- d) Applications of CBED and EDXS to rare earth permanent magnets.
- e) Channelling enhanced microanalysis.

1. Introduction

The characterisation of materials both physically and chemically is essential in order for continued progress to be made in understanding materials performance and to improve existing materials, or to design new materials. Whilst it is now possible to actually achieve interpretable atomic resolution in images of crystalline solids (e.g. refs. 1-3), high resolution quantitative spectroscopic chemical analysis is still fraught with difficulties, mostly associated with detectability (signal to noise ratios), interpretation of spectra (or absorption edges), specimen contamination and damage, etc. That is, the problem is a complex interactive one involving the instrument, specimen, detectors, and analysis. Direct spectroscopic microanalysis involves inelastic scattering of electrons by the specimen and suitable detectors to monitor the resultant events, e.g., x-ray emission, or energy loss electrons, whereas, indirect information can be obtained from diffraction, e.g., convergent beam analysis, or with care by lattice imaging. The principles may be illustrated by fig. 1. Not all of these scattering events are easily monitored, however, (e.g., the auger signal occurs after a three electron scattering event and hence is useful for elements with $Z > 3$ so that Li is not detected) and so for general applications x-ray spectroscopy by energy dispersive analysis (EDXS) electron energy loss

spectroscopy (EELS), microdiffraction with convergent beams (CBED) and high resolution imaging are most frequently used. The basic methods and background are given in the literature (e.g., refs. 3-5), including the use of CBED or EELS for estimating foil thickness, a necessary condition for quantitative analysis. Although these techniques are now quite well known, and it is not necessary to review them in detail, a brief discussion of the current status of EDS, EELS, and CBED may be useful for the practical microscopist interested in materials.

2. Summary of Limitations/Advantages

a. Energy Dispersive X-Ray Spectroscopy: (EDXS)

A typical energy dispersive x-ray spectrum is sketched in fig. 2a. The spectrum is simple in form and lends itself to relatively easy interpretation and quantification. Routine Gaussian deconvolution techniques permit accurate quantification of even severely overlapped peaks. The background is weak and well tested expressions have been developed to model it. The instrumentation is uncomplicated and the detection is normally done in parallel over the whole energy range. This allows for quick and routine application. However, the accuracy of the quantitative data is ultimately determined by the counting statistics of the x-ray collection process and, hence, counting times on the order of 200-300 seconds might be necessary for true elemental analysis.

The use of a Be-window detector normally limits the application of EDXS to elements of atomic number $Z \geq 11$ unless ultra-thin window (100 nm of Al coated on a thin polymer film) detectors ($Z \geq 6$) or windowless detectors are used. For elements of $Z > 40$ problems exist with excitations in the Si detector unless Ge detectors are available. The spatial resolution is largely determined by the beam broadening which is a function of the acceleration voltage, the average atomic number of the sample, and its thickness. For a point incidence of 100 keV electrons on a 50 nm thick sample, the broadening has been calculated to be 1.8 nm for carbon and 17.3 nm for gold. The sensitivity of the technique is specified in terms of the Minimum Detectable Mass which is approximately 5×10^{-20} g for elements with atomic number in the range $10 < Z < 40$ for a 100 sec. counting time and an incident current density of 20 amp/cm² and an acceleration voltage of 60-100 keV. (6).

Apart from the recently observed phenomenon of Coherent Bremsstrahlung (7) and the technique of Channelling Enhanced Microanalysis (8) that provides crystallographic information, EDXS is mainly used to obtain microanalytical information from the sample. The energy resolution is very poor, 150 eV for Mn K α radiation, largely because of the complex nature of the interaction of the x-rays with the silicon (detector) crystal lattice and the competition between the various energy dissipation processes. Since the characteristic x-ray emission is a secondary event, only a fraction of the inner-shell ionizations result in such emissions. This fraction is termed the fluorescence yield (w) where $w \ll 1$ and is ~ 0.1 for low energy emissions. Appropriate precautions to avoid spurious detections due to secondary fluorescence have to be well established for the particular TEM and EDXS system (9). Further, the geometric collection efficiency is very small ($\sim 1\%$) and is a function of the solid angle projected by the detector. This technique is, at present, incompatible

with Ultra High Vacuum specimen chambers. Finally, because of the orientation dependence of the x-ray signal it is most important to collect the x-ray spectra under conditions where no Bragg reflections are excited (10). The same is, of course, true for EELS. (see sec. 3e.)

b. Electron Energy Loss Spectroscopy: (EELS)

A typical EELS spectrum e.g., fig. 2b, has absorption edge characteristics of the elements present and is rich in information. It is possible, in principle, to perform microanalysis for all elements in the periodic table, i.e., from hydrogen to uranium, using this technique and it is particularly applicable for the analysis of low atomic number elements. EELS will detect light elements because the energies of the absorption edges are separated well enough to be resolved by the available spectrometers, e.g., the K edges of boron (188)ev, carbon (284)ev, nitrogen (400)ev, oxygen (532)ev, magnesium (1305)ev, aluminum (1560)ev, silicon (1839)ev. Hence, this technique truly complements EDXS. However, existing methods for quantitative microanalysis by EELS seem to be valid for thin specimens only and the accuracies are often limited by the uncertainties in the modelling and fitting of the background (11). In principle, the errors due to plural (elastic as well as inelastic) scattering in thick crystals can be reduced by deconvolution. In general, the Fourier-log deconvolution (12) should be used as this has been found to give the best results. Further, superimposed on the overall features of the edge is a complex fine structure that provides information on the chemical bonding (ELNES) and the coordination and local crystallography (EXELFS). These techniques are in their nascent stages and much work needs to be done before they can be routinely applied. The versatility of EELS is further enhanced by recent developments in imaging using inelastically scattered electrons such as energy filtered imaging and Z-contrast imaging (13,14). This technique detects a primary event, it is neither limited by fluorescence yield nor is it affected by secondary fluorescence. The former in combination with good geometrical collection efficiencies (0.1-1) gives a large number of counts in the region of interest and hence, good statistics are obtained. The latter enhances the spatial resolution of the analysis which is then limited only to the diameter of the electron probe, particularly for thin samples. Further, good energy resolutions 1-5 ev are routinely obtained. For state of the art spectrometers, this is mainly a function of the energy spread in the electron source. From the microanalysis point of view, the sensitivity of the technique is specified by the Minimum Detectable Number of atoms (MDN). Currently achievable values for a 50 nm thick specimen range from 4×10^3 for Li(K) to 1.2×10^5 for O(K) (15).

The major difficulty with EELS is that the complex physical processes that contribute to a typical spectrum also increase the difficulty of interpretation. The background is strong and is an integral part of the spectrum. No consensus on the expression for modelling the background has as yet been arrived upon, however, one of the form AE^{-r} (where E is the energy loss and A and r are arbitrary constants obtained by curve fitting) is now generally accepted. As mentioned earlier, multiple scattering is a common feature, (except for very thin specimens) and for almost all cases deconvolution of the spectra may be necessary. As of now only serial detection (i.e., channel by channel counting) is possible and hence the

acquisition of a typical spectrum is time consuming, for at any given time, 99.9% of the electrons go undetected. However, a number of parallel detection systems are currently in commercial development.

Perhaps the most promising fields for EELS applications are in electronic materials and ceramics. In the latter case, identification of anions such as carbon, nitrogen and oxygen is often of great significance such as in materials sintered or hot pressed with sintering aids. One example is SiC sintered with the addition of carbon. While an optimum addition of carbon enhances the sintering process, an excess amount can impede the densification process. The use of electron microscopy and EELS has been used to identify excess carbon and its form in a sintered SiC compact. These results are shown in fig. 3 which reveals the power of EELS, not only for elemental identification, but also for crystallographic characterization based on absorption edge shape. In this case, excess carbon was identified as being in its graphitic form.

It must also be pointed out that the experimental limitations of both of these spectroscopy procedures in the electron microscope are compounded by problems of contamination and radiation damage of the specimen itself. The detection of light elements in ceramic specimens is less of a problem than in metals, especially if the latter are prepared electrochemically.

c. Convergent Beam Diffraction

The convergent beam diffraction (CBD) method, fig. 4, (described amongst others by Steeds (16) and Williams (5)) offers several advantages over conventional (selected area) diffraction. Much smaller areas can be sampled (typically tens of nanometers in diameter as opposed to 0.5 μ m) while also providing symmetry information (enabling phase identification) and a more sensitive measure of lattice parameter (typically 1 in 10^3 or 10^4 , compared with 1 in 10^2 for selected area diffraction). Most sensitive to changes in crystal symmetry are the intensities of reflections in the Higher Order Laue Zone (HOLZ) rings, for which the large magnitude of g in the structure factor term $\exp(2\pi i g \cdot r)$ allows small displacements in atomic positions (r) to create noticeable intensity changes. The geometry of HOLZ diffraction makes the relative position of HOLZ deficiency lines within the central CBD disc very sensitive to lattice parameter.

In the application of CBD, considerable time and effort is demanded of the operator. The incident beam must be exactly aligned with the zone axis, and the pattern focussed exactly at the back focal plane of the objective lens, for the true symmetry to be shown. Specimen and microscope column cleanliness must be maximised to prevent the otherwise rapid growth of contamination layers under the beam. Contamination can mask the details of a CBD pattern with diffusely-scattered intensity within the time taken to achieve the necessary orientation and focus conditions. A cold-trap anticontaminator is essential, and a cold specimen stage will assist further by reducing the mobility of contaminant molecules across the specimen surfaces.

The extent to which CBD is useful can depend on the properties of the material itself. The large g vectors involved magnify the effect of the Debye-Waller factor, making HOLZ intensities very weak for some materials

except at liquid nitrogen or helium temperatures. HOLZ intensities will similarly be weakened for materials with large densities of "frozen-in" disorder, i.e., point defects. Indeed, some materials will show weak HOLZ effects at some zone axes simply because the reciprocal lattice spacing is large along those directions.

The limit to the spatial resolution of the method is tied to the requirement of a minimum thickness for HOLZ reflections (which have very long extinction lengths), typically around 100 nm. The inevitable broadening of the beam by scattering events within this distance may increase the area effectively analyzed to several times the probe size, depending on atomic number. Since smaller probes generally contain a lower current, and can give extremely faint CBD patterns, a larger probe than the minimum is often used, with only a small decrease in the overall spatial resolution after broadening. As in all cases, sensitive specimens may be difficult to analyse because of radiation damage. These problems are intensified if high beam currents are employed over relatively small areas.

3. Some Research Examples

a. Steels

Perhaps the most important yet most difficult elements to quantify in many steels are the interstitial elements; carbon, nitrogen, and oxygen, and of course, hydrogen remains undetectable. The main substitutional elements, chromium, manganese, molybdenum etc., can all be detected by EDXS. As discussed above, the limitations for the lower atomic number elements ($Z < 11$) are that detection is limited by the low x-ray signal unless windowless detectors are used whereas, at the higher end ($Z > 50$) problems are encountered due to ionization events in the detector itself. Although in principle the interstitial elements can be detected by EELS, the problem is complicated by the contamination occurring during examination of the specimen and also due to the oxidation layers that form on the surface (e.g., during foil preparation). It may be concluded that EELS is not applicable for detecting carbon levels much below 0.5wt% unless the contamination problem is overcome. The problem has been addressed in detail by Sarikaya et al. (17,18) and over the years a variety of techniques have been applied. The approach is illustrated in fig. 5, whereby combined microanalysis, microdiffraction and atomic spectroscopy using a special field ion atom probe instrument (17) shows clearly the partitioning of carbon that occurs in low and medium carbon steels quenched from austenite to yield lath martensite with interlath retained austenite as shown at the top of the figure. These data support the earlier results of Rao et al. (19) who used lattice imaging to estimate carbon levels in these types of steels at a time when direct spectroscopic methods were not available. What this example illustrates is the principle of research to attack a problem with as many techniques as possible rather than relying on one method, even if it is highly refined.

Another important problem of solute atom partitioning is that occurring during intercritical annealing treatments in the ferrite-austenite phase field involved with dual phase low carbon steels. The partitioning of elements affects the hardenability of the austenite phase since such steels are quenched and so it is important to evaluate this. Current

research on Fe/Si/C, Fe/Mn/C, Fe/Al/C and others indicate that appreciable partitioning of Mn occurs but depending on temperature and other elements, very little partitioning is found for Si and a little more for Al (e.g., fig. 6). The partitioning is a function of time and temperature. Detailed information on interstitial element partitioning in dual phase steels is not yet available. If microalloying elements are present, subsequent precipitation may occur in ferrite (fig. 7) and this can greatly affect mechanical properties (20,21). Since it is very difficult to carry out EDXS analysis of such small precipitates directly in thin foils, it is best to use carbon extraction replicas. Figure 8 is an example showing that these small precipitates are rich in vanadium (in this case).

b. Zirconia Ceramics

Zirconia (ZrO_2 -monoclinic at ambient temperatures) as a material or as a constituent in zirconia-oxide ceramic composites is of great current interest due to its beneficial toughening contributions (22). Several projects are being investigated including zirconia partially stabilized with various oxides, as well as zirconia dispersed in mullite. Zirconia doped with 2.3 mol % Y_2O_3 forms tetragonal zirconia polycrystals (TZP). Reflections which are forbidden in diffraction patterns from the tetragonal and cubic polymorphs are frequently observed, and are seen to arise from domains of altered crystal within the tetragonal grains. In some areas, the spacing of reflections is halved along one direction as in the [100] CBD pattern in Figure 9a. A weak extra HOLZ ring of reflections indicates the same effect along the beam direction. A dark field image taken in the arrowed extra reflection (Fig. 10) shows the altered area. The remainder of the grain exhibits the normal tetragonal [100] CBD pattern (Fig. 9b). In other areas, the spacing of reflections along 100 and 010 becomes one quarter, as in Figure 11, which shows [100] CBD patterns from adjacent parts of one grain, and shows the effect occurring on mutually orthogonal rows of reflections. A high magnification image (Fig. 12) shows that this grain consists entirely of domains showing a four-fold increase in lattice spacing, with considerable faulting.

Possible explanations for these effects are that new phases have formed, or that ordering within the tetragonal phase is occurring. Transformation to the monoclinic structure would also introduce a halving of the reflection spacing, but the patterns examined show an insufficient set of reflections for this [23]. EDXS analysis of the area in Figure 12 shows insufficient yttrium for the nearest intermediate compound, YZr_4O_9 , to be present (Figure 13). Instances of ordering have previously been attributed to the formation of such intermediate compounds [24,25], although these are noted as growing very slowly, even for high yttria contents (up to 40%). Both an orthorhombic [26] and a rhombohedral [27] phase have been reported within this system for certain Y_2O_3 contents below 10 mol %, although neither would account for the observed diffraction patterns. It is likely that electrostatic forces between yttrium ions and oxygen vacancies have led to ordering. The latter, which are the more mobile, probably play the dominant role.

Quenching rates and particle size effects, among others, may complicate comparisons between the results of different workers, but it is becoming apparent that the three conventional polymorphs of ZrO_2 are insufficient

to describe the material in its stabilized or partially stabilized forms.

c. γ -Fe₂O₃ Particles in Recording Media

γ -Fe₂O₃ particles were developed more than half a century ago and today these are still the most widely used magnetic materials for disks and tapes. Although many structural studies of γ -Fe₂O₃ have been made by many investigators, (e.g., refs. 28-38), 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 data for the crystal structure have not yet been obtained. Among the results, it is generally believed that γ -Fe₂O₃ has a tetragonal structure of $c/a = 3$ with $a = 8.33$ Å due to the fractional nature of iron cation vacancies. Because of these factors convergent beam electron diffraction (CBED) has been used to study individual particles. Extra lines at 110, 210, and 211 observed in X-ray diffraction suggest that a change in symmetry from a face-centered cubic lattice to a primitive lattice has occurred. This finding is also supported by the CBED results, as shown in fig. 14, in which reflections forbidden by the fcc structure such as 100, 110, 210 etc. are present. For convenience, fig. 14 is indexed in terms of the Fe₃O₄ unit cell. Figure 15 and 16 are primary CBED zone axis patterns of two different specimens as used for X-ray analysis. Both γ -Fe₂O₃ samples clearly showed the same crystal symmetry. Since the internal structure of the discs cannot be seen, the crystal symmetry must be determined from analysis of the HOLZ symmetry. As shown in fig. 17, the HOLZ symmetry is more easily resolved when smaller condenser lens apertures are used (e.g., 50 m). From fig. 17, it can be seen that the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ zone axis patterns show the 4 mm, 2mm and 3m symmetries, respectively. From tables published by Buxton et al. (39) 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 (28, 34, 35). Due to the small particle size, no structure is visible in the zero order reflections and the space group of the material cannot be determined. However, from the knowledge that γ -Fe₂O₃ has a primitive lattice and m3m point group, there are only four 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 wave-length, R is the radius of the high order Laue ring, and L is the camera length (see fig. 4). By using the above equation, the γ -Fe₂O₃ 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. Figure 18 is a series of CBED $\langle 110 \rangle$ 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 $\langle 100 \rangle$ and $\langle 111 \rangle$ zone axes as well and the resultant structure continues to have the m3m point group symmetry, as shown in

Figure 19. The same pattern as Figure 18 was obtained after re-examining the same area 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 (40). However, electrons may transfer, by ionization damage, sufficient momentum to enhance cation diffusion, especially in a high defect density material such as $\gamma\text{-Fe}_2\text{O}_3$. 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 (40). 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.

d. Microstructure and Coercivity Mechanism in Fe-RE-B Permanent Magnets.

The microstructure and microanalysis of Fe-Didymium-B permanent magnets are being studied in order to understand the dominant coercivity mechanism in this class of magnets. One composition is as follows: Fe-Didymium (80%Nd-15%Pr-5%Ce)-1%B. Magnetic measurements indicate that the magnetization reversal is predominantly by a nucleation mechanism. Since the coercivity is extremely sensitive to microstructural changes, the microstructure is being investigated in detail. The overall microstructural features as well as the diffraction patterns from the grains and intergranular phase, and microchemical analyses obtained by EDXS are shown in fig. 20. The magnetic grain is a tetragonal $(\text{RE})_2\text{Fe}_{14}\text{B}$ phase, which is imaged here in the [001] orientation. At all the triple grain junctions, and at most two-grain boundaries, an fcc, non-magnetic phase exists. This phase is rich in Nd, Fe, Ce and also has a considerable amount of oxygen. Previous workers interpret the intergranular phase as a bcc phase, but this is now believed to be an artefact of foil preparation. Lorentz microscopy shows that domain wall pinning at the non-magnetic intergranular phase is the main cause of the coercivity. Thus, the existence of this phase appears to be important in achieving high intrinsic coercivity values.

e. Channelling Enhanced Microanalysis

A technique that enhances the potential of energy dispersive x-ray microanalysis in materials characterization called channelling enhanced microanalysis (CEM) has been developed (Fig. 21). This technique, based on the orientation dependence of electron-induced characteristic x-ray emissions, has been used to obtain crystallographic information such as preferential site occupations from very small local regions of thin film and bulk magnetic materials. In general, occupations of crystallographic sites for levels of doping equivalent to 10^{20} atoms/cm³ with an accuracy of 2-5% can be routinely determined by this technique.

For crystalline materials, an incident-plane wave of electrons under conditions of strong dynamical scattering sets up a standing wave within the crystal unit cell. The intensity modulations of this standing wave within the crystal unit cell are a function of the incident beam orientation and the accelerating voltage. As the scattering events (like inner shell excitations) that lead to characteristic x-ray production are

highly localized, the x-ray intensities in turn, are also strongly determined by the orientation and the acceleration voltage. For a given acceleration voltage or wavelength of the incident wave, it has been shown that this orientation dependence of the characteristic x-ray emission can also be used as a probe for determining specific site occupations of elemental additions in single crystals. (41-45)

Two different formulations based on the crystal structure to be analyzed have been developed (45). The crystal structures were classified either as layered or non-layered. A layered structure was defined as one in which the crystal structure can be resolved into alternating non-identical parallel planes, each plane containing one or more specific crystallographic sites.

The application of this technique to a general non-layered crystal structure requires a theoretical prediction of the characteristic x-ray production as a function of incident beam orientation because specific-site sensitive orientations cannot be determined by mere inspection of the crystal structure. Hence, a real space formulation considering flux loss from the incident beam and under the assumption of highly localized inner shell excitations was developed for x-ray production in thin crystals. Applying this theory, a $g=121$ systematic row was predicted to be the specific-site sensitive orientation for thin epitaxially grown garnet films of nominal composition $Y_{1.7}Sm_{0.6}Ly_{0.7}Fe_5O_{12}$. Experimentally observed data were then refined using a constrained least squares analysis to give probabilities for the occupation of rare-earth additions in the different crystallographic sites of the unit cell. Thus, it has been shown that in these compounds, Lu^{3+} and Sm^{3+} additions prefer octahedral site occupation with a probability >95% (46, 47).

For layered crystals it has been shown that the appropriate orientations can be determined by inspection. However, the analysis (ref. 41) requires an a priori knowledge of the distribution of some reference elements, along with some implicit assumptions about the crystal structure. A general formalism, with the underlying idea that additional relationships can be generated by performing these experiments at an appropriate number of orientations and which overcomes some of the limitations has been developed (43). Based on this formalism it was determined that 88.5% of the Mn atoms and 85.1% of the Fe atoms occupy sites in the mixed planes of the $Sm_2(Co,TM)_{17}$ compound (42).

Finally, a systematic experimental study has been carried out recently to determine the combined effect of acceleration voltage and incident beam orientation on the characteristic x-ray production in thin crystals (47). For $MgAl_2O_4$ (spinel), it has been shown that the orientation dependent characteristic x-ray emissions undergoes an interesting reversal in character above a particular voltage labelled as the "inversion voltage". This "inversion voltage" has been experimentally determined to be ~270Kv for this compound. A physical interpretation of this phenomenon in terms of the localization of the Bloch wave in the crystal unit cell has also been suggested. However, the theory does not seem to completely characterize the results. Further, in combination with theoretical calculations (49), this inversion voltage behavior has been shown to be

different from the conventional critical voltage effect (48). From the microanalysis point of view, it has been shown that in order to obtain an analysis that is truly representative of the chemical constitution of the sample, it is essential to systematically tilt the crystal to an orientation at which no lower order Bragg reflections are excited.

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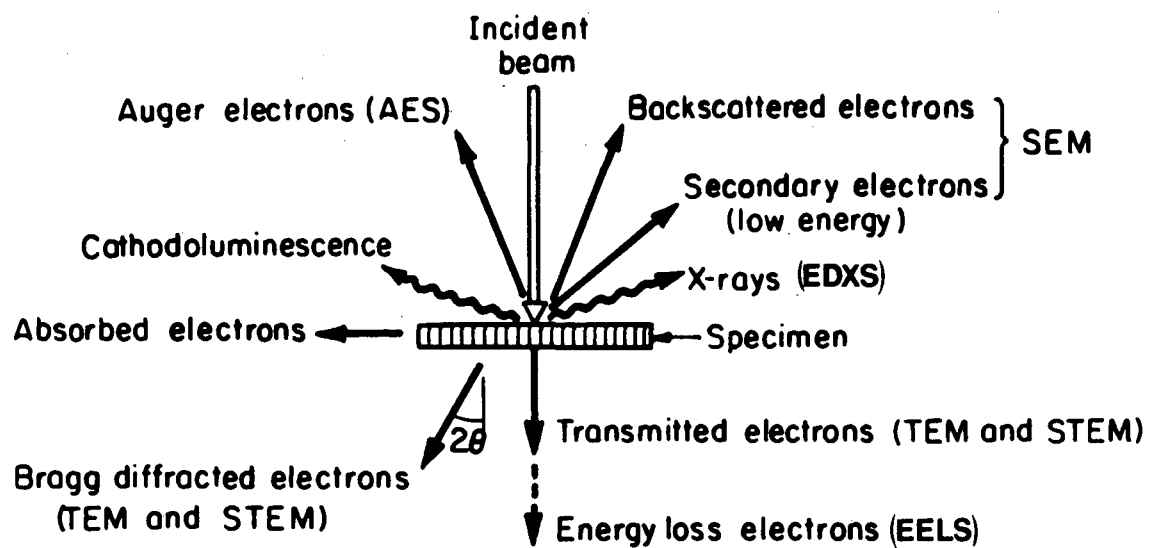
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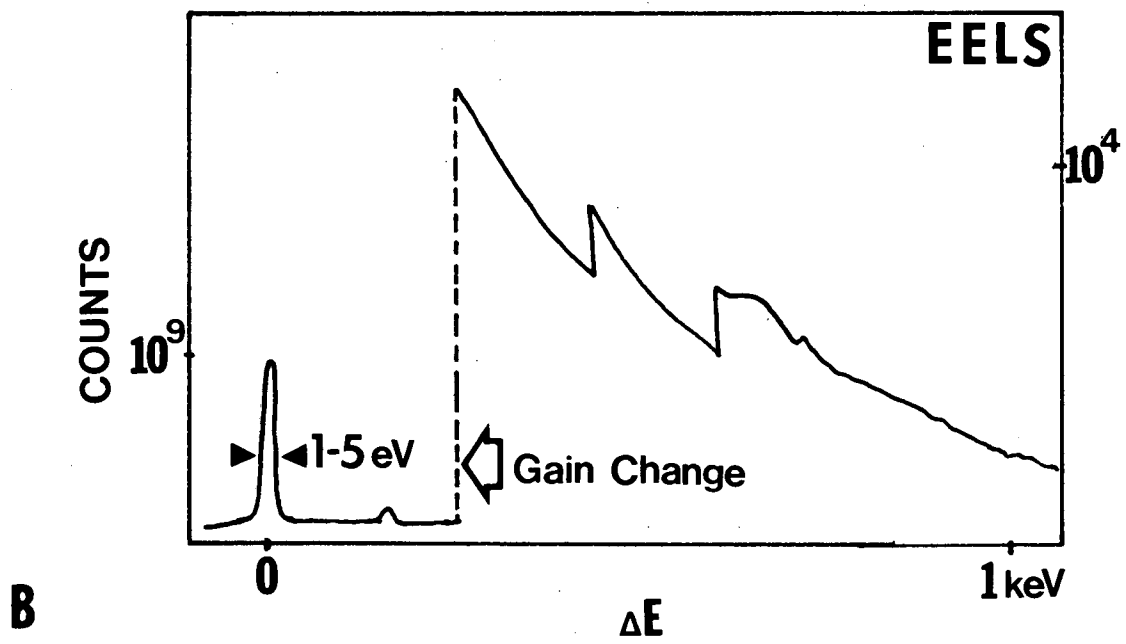
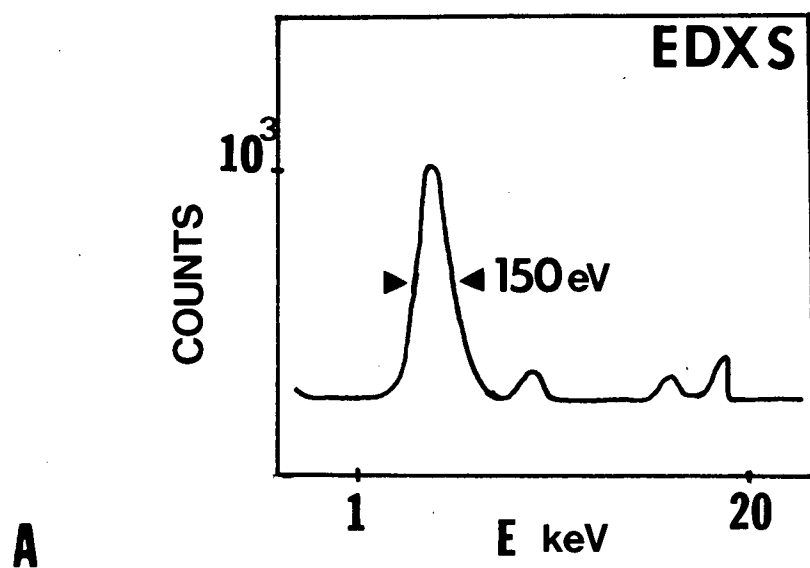
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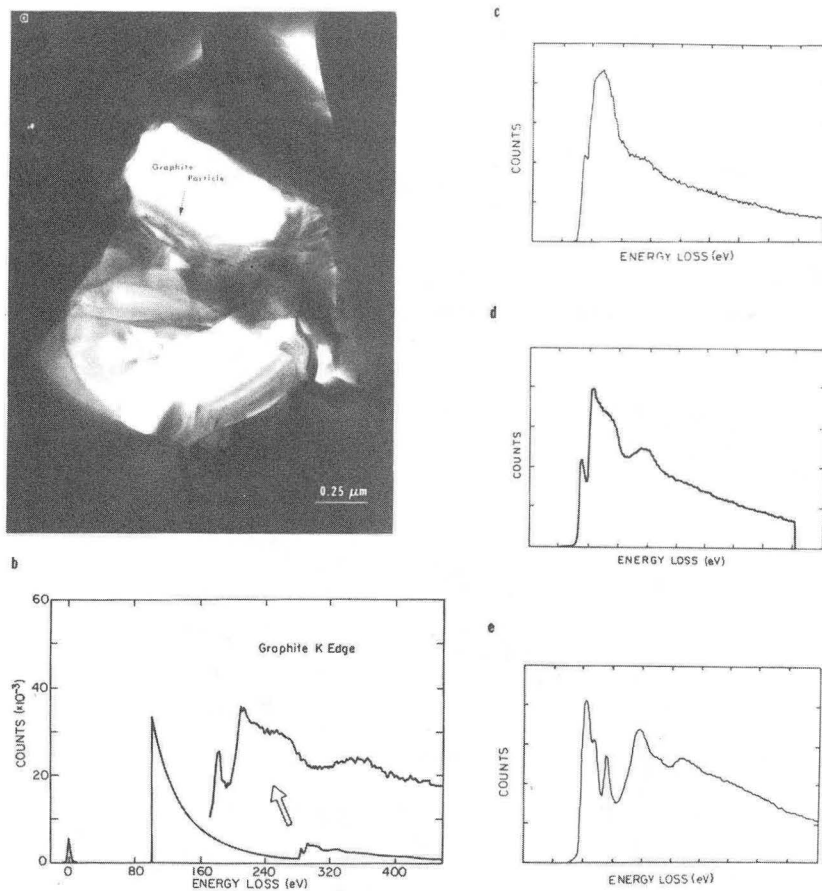
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Fig. 1



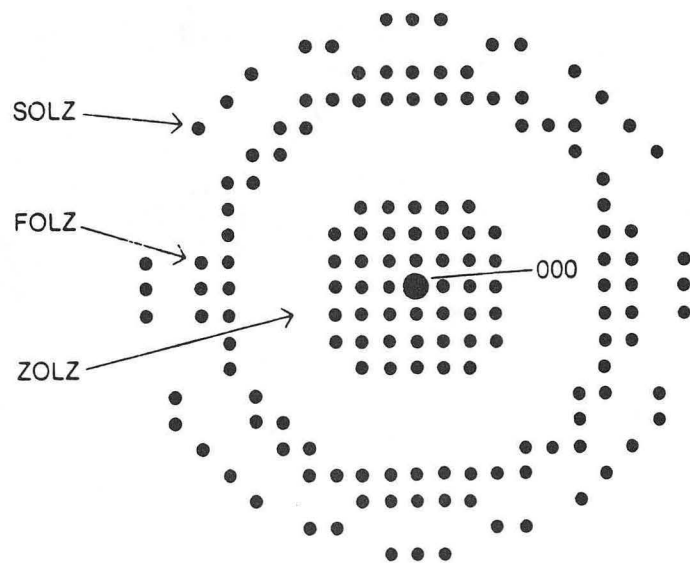
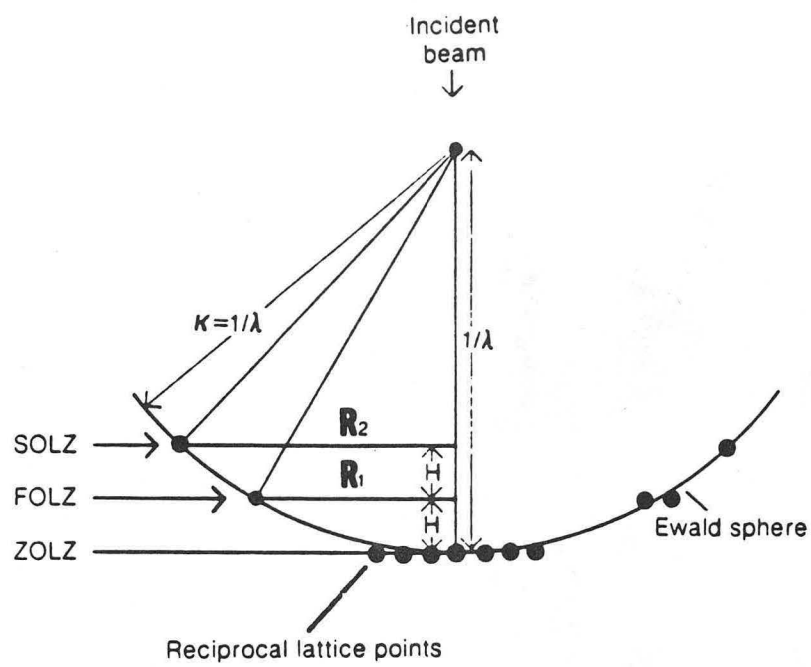
XBL 858-3661A

Fig. 2



XBB 858-7008

Fig. 3



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

XBL 858-3751

Fig. 4

CARBON PARTITIONING IN RETAINED-AUSTENITE IN LATH-MARTENSITIC STEELS

TRANSMISSION ELECTRON MICROSCOPE - IMAGE STUDIES

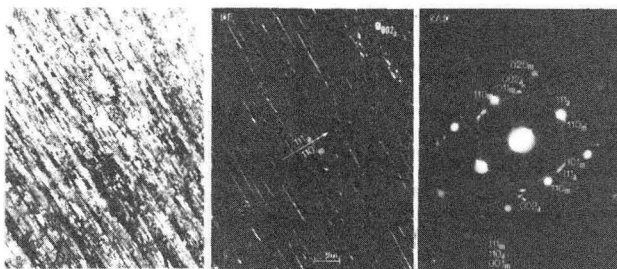
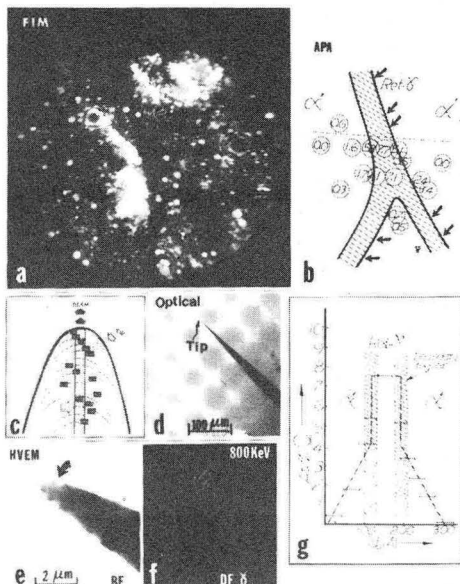


FIGURE 1 - (a) BF and (b) DF images illustrating the general appearance of thin films of Ret- γ at the martensite lath boundaries (0.5 at.% C steel). (c) Composite SAD pattern of martensite (m) and austenite (a).

The microstructure consists of dislocated lath martensite with fairly straight boundaries and thin film Ret- γ at the lath-like martensite crystal boundaries. DF micrographs (Fig. 1) shows an extensive amount of Ret- γ (5 vol.%) even at this low carbon level. The existence of this high temperature phase at low temperatures is attributed to several mechanisms in which interstitial C stabilizes the austenite. (i) Chemical stabilization: Diffusion and partitioning of C in Ret- γ decrease the local M_s temperature and inhibit further transformation. (ii) Thermal stabilization: During quenching interstitial C forms dislocation atmospheres in α' and at the α'/γ interface, pinning the dislocations and suppressing interface motion. (iii) Mechanical stabilization: Part of the austenite to martensite shear transformation strains is accommodated by soft γ which deforms extensively to prohibit the transformation.

The average C concentration in Ret- γ can be determined by measurements of shift in positions of the holz lines in CBED patterns in relation to the change in the lattice parameter of the Ret- γ , due to C: $(\Delta a_c/a_{ref}) = (2/3)[(p/q_c) - (p_{ref}/q_{ref})](9/115)^2$. Ni (99.99% with $a_0 = 3.5238$) was used as a reference, and results cross-checked with Cu (99.999% with $a_0 = 3.6150$). For the example shown in Fig. 2, ΔC at.% = 4.9 ± 0.6 (at.% C alloy = 0.7) taking $a_{Ret-\gamma} = 3.555 + 0.044X$ (w/o C).

FIELD ION MICROSCOPY - ATOM PROBE ANALYSIS



Atom probe analysis provided direct quantitative determination of the C distribution in α' and Ret- γ at 20-30 Å resolution. Considerable C enrichment occurs in Ret- γ - direct evidence of chemical stabilization (figs. 3-4). Detailed measurements of C distribution in a thicker Ret- γ film (fig. 4) gave an average concentration of 3.0 at.% and up to 8.5 at.% at the $\alpha'/\text{Ret-}\gamma$ interface (Thermal stabilization). The extent of deformation (Mechanical stabilization) is discernible in TEM micrographs in fig. 4. There is no apparent change in distribution of substitutional alloying elements (Cr and Mn, fig. 4) in α' and Ret- γ . Hence changes in the amount of Ret- γ with alloying elements are attributed to their interaction with C influencing its mobility. Thus the overall stability of thin film Ret- γ is due to effects of several mechanisms.

FIGURE 3 - (a) FIM image of Ret- γ . (b) Regions of APT analysis. (c) Illustration of the analysis of subsurface regions by field evaporation. (d) Low magnification image of the tip. (e) WTEM BF and (f) DF images reveal Ret- γ . (g) Concentration profile for C across the interface.

Retained austenite (Ret- γ) has been identified in a number of carbon containing lath martensitic steels with M_s and M_f temperatures well above room temperature. Because of its beneficial effects on the mechanical properties (especially fracture toughness) of HSLA steels the influence of interstitial C in stabilizing the γ has been studied in detail using TEM, CBED and FIM-APA techniques.

Steels were austenitized at 1100°C, and oil quenched. TEM foils were prepared by electropolishing in chromic acid at room temperature (RT), and Cu and Ni standards in 25% HNO_3 in $\text{CH}_3\text{-OH}$ at -30°C. Some steel foils were etched for CBED by "dipping" in 15% HClO_4 -5% $\text{C}_2\text{H}_5(\text{OH})_2$ - CH_3COOH at -25°C. FIM tips were electropolished in 25% HClO_4 in $\text{CH}_3\text{-COOH}$ at RT.

CONVERGENT BEAM ELECTRON DIFFRACTION

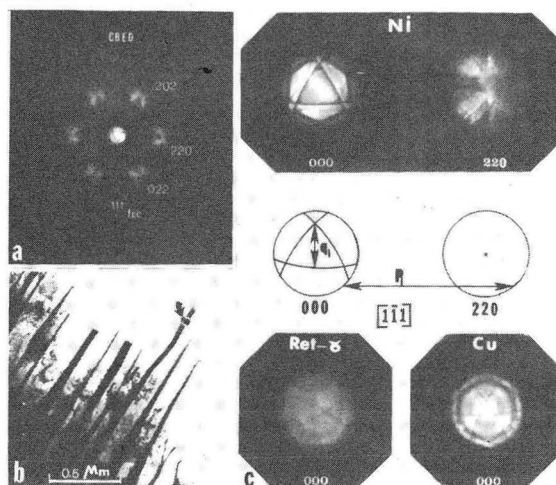


FIGURE 2 - (a) Nickel (fcc) 111 CBED-pattern at 100 kV reveals trigonal symmetry. (b) DF image, from a specially prepared foil, shows the Ret- γ films extending into the perforation. (c) Discs formed by forward scattered beams from Ni, Ret- γ , and Cu (note q_c and p_c).

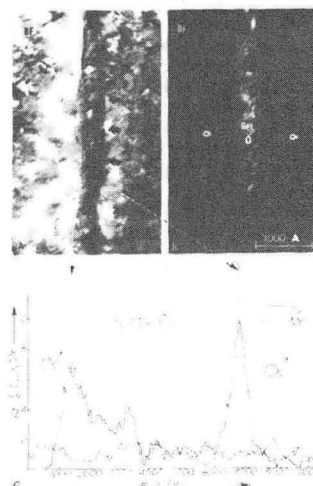
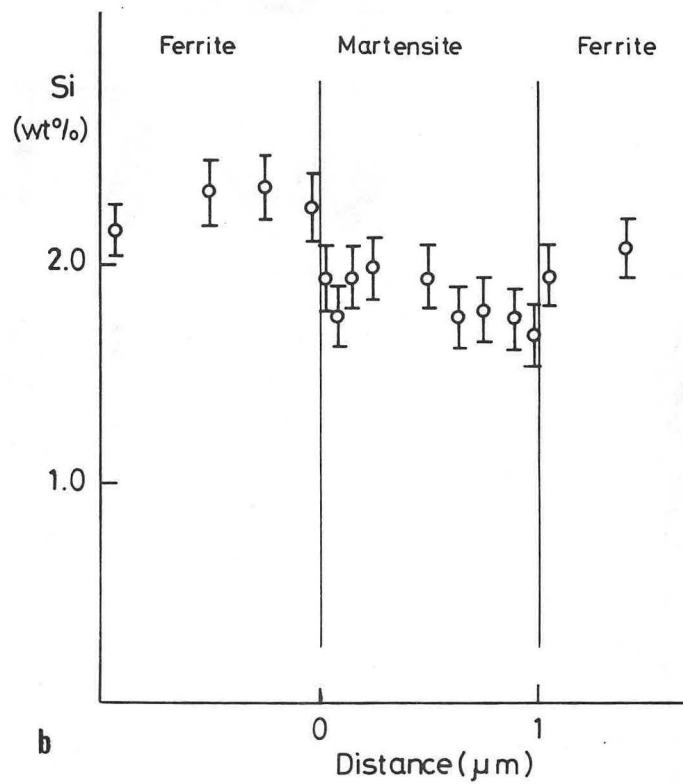
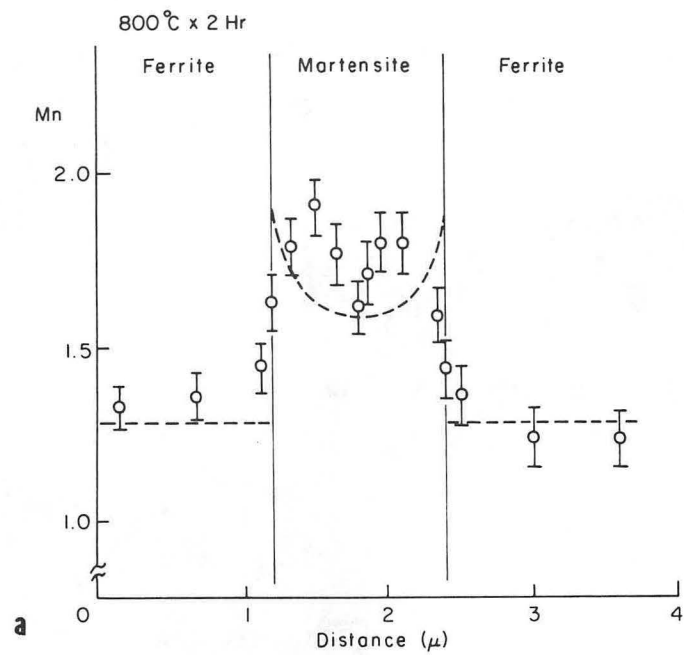


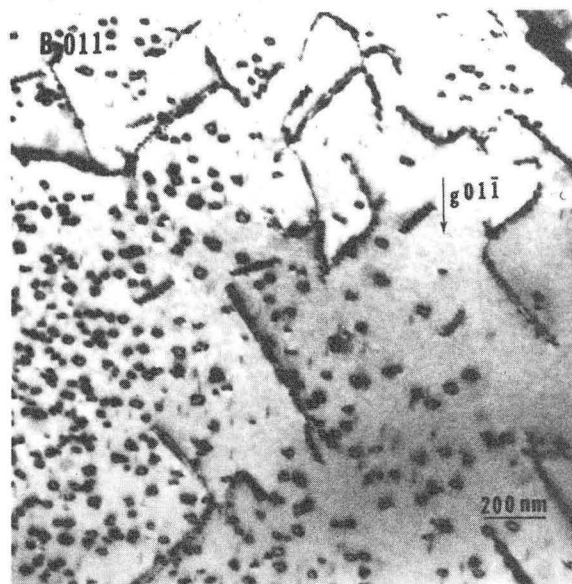
FIGURE 4 - (a) BF and (b) DF TEM images reveal the extent of deformation of Ret- γ . (c) Concentration profiles for C, Cr, and Mn over Ret- γ film by APT from 1.25C-3Cr-25Mn steel.

XBB 817-7029



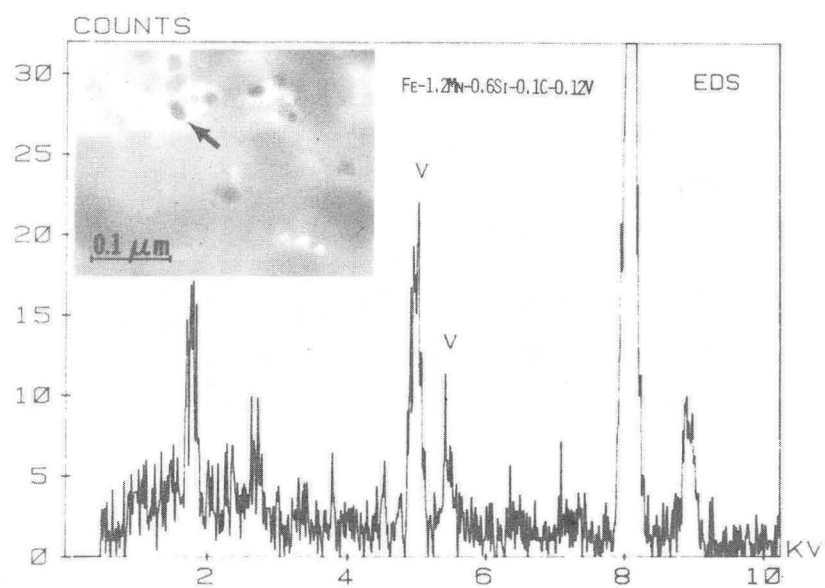
XBL 858-3668A

Fig. 6



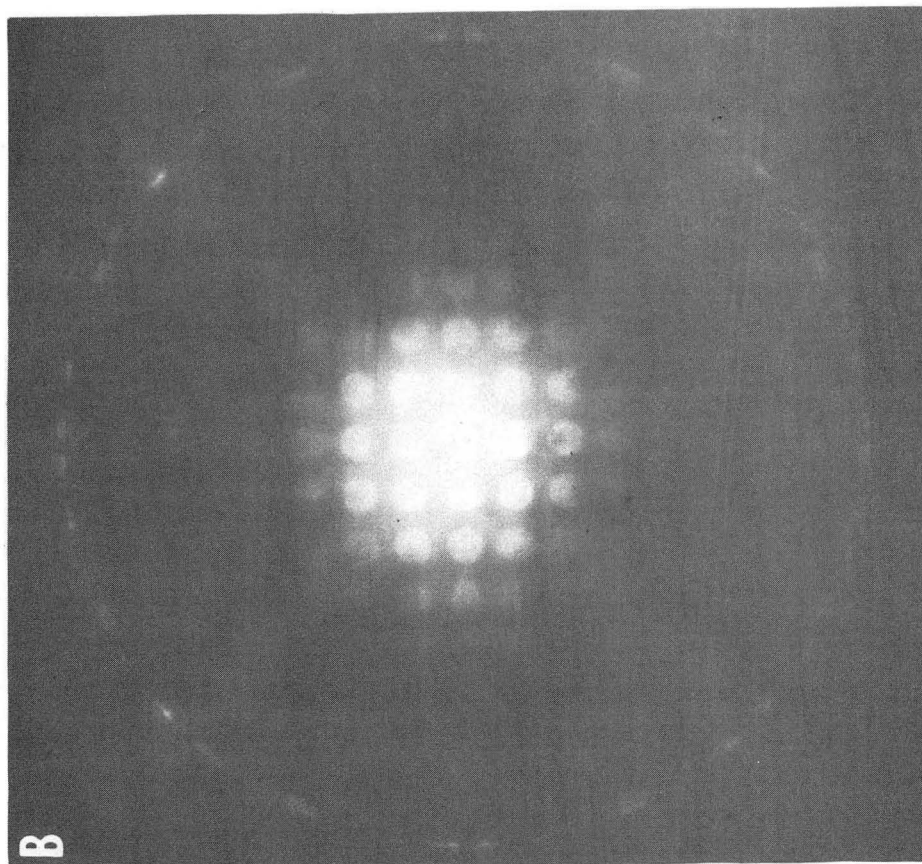
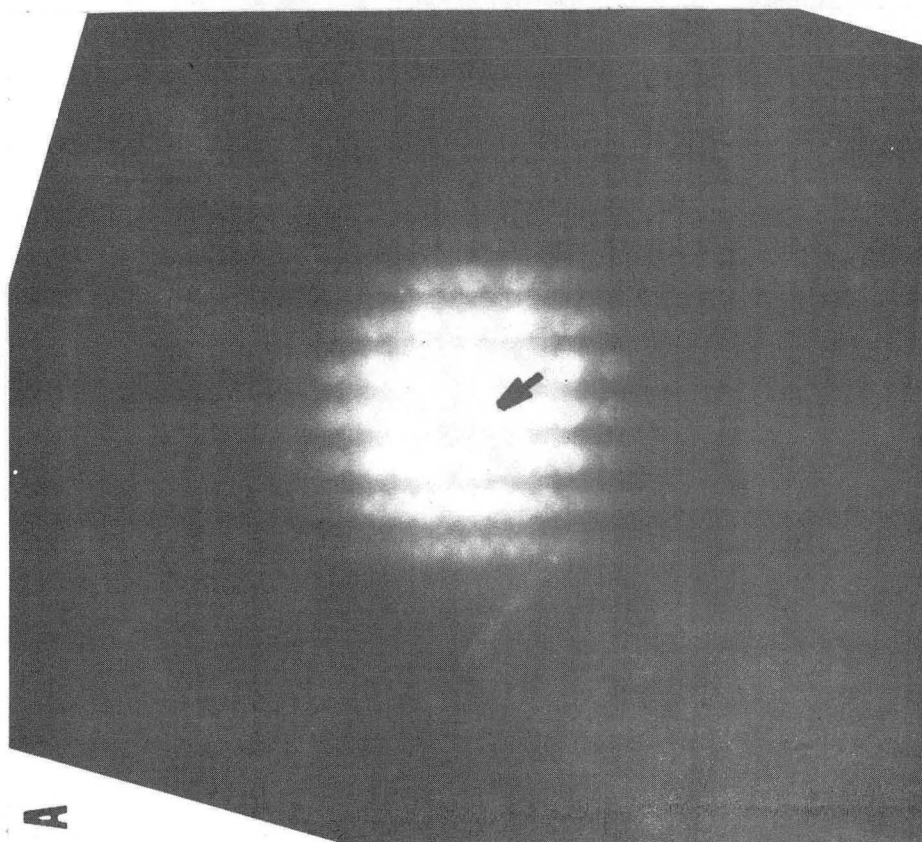
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Fig. 7



XBB 823-2182

Fig. 8



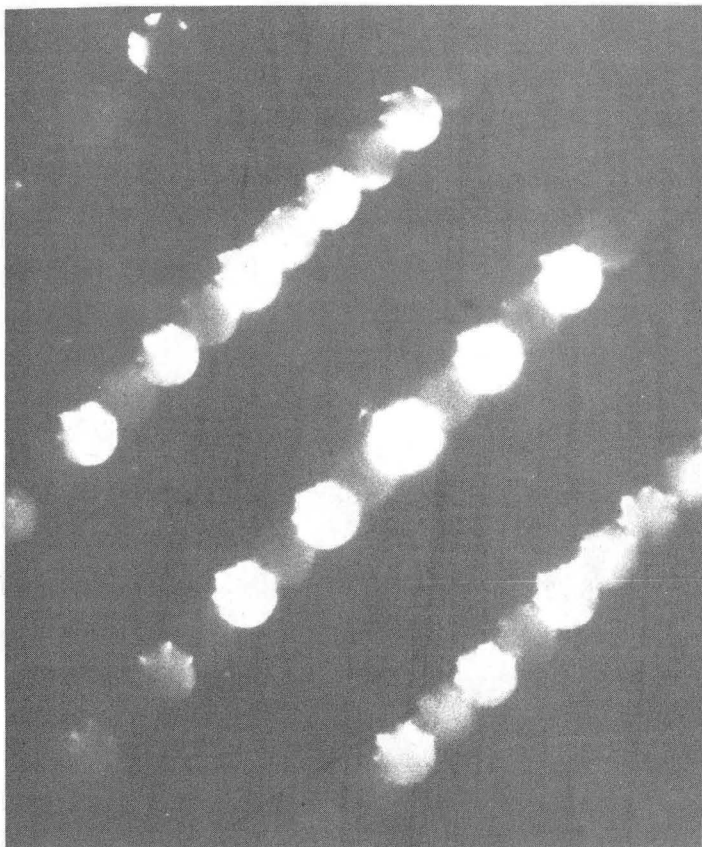
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Fig. 9



XBB 857-5435

Fig. 10



XBB 855-3888

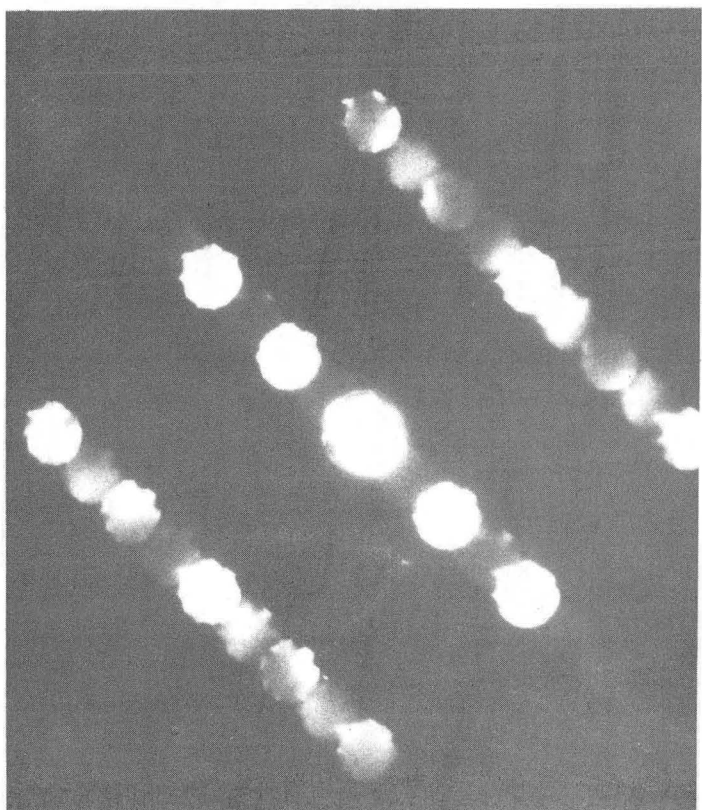
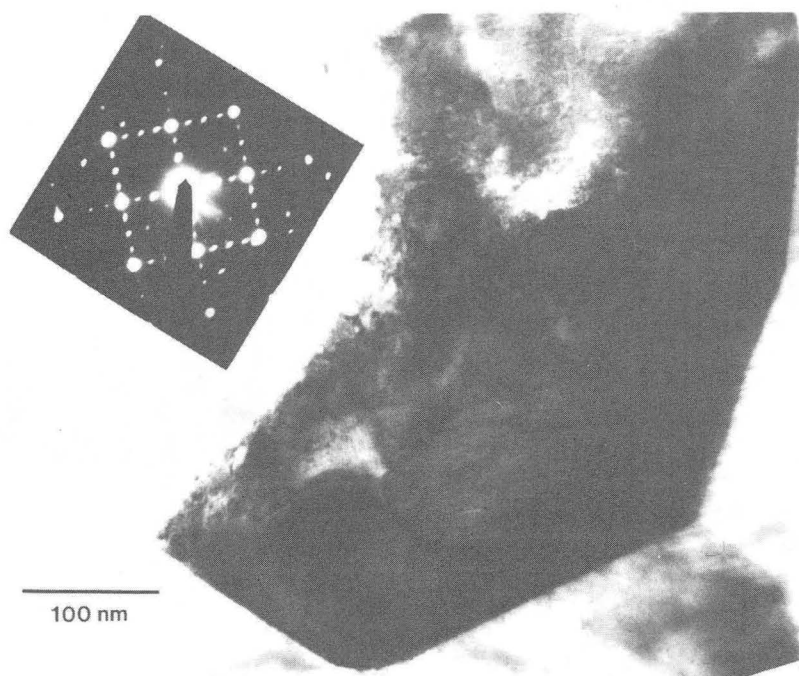
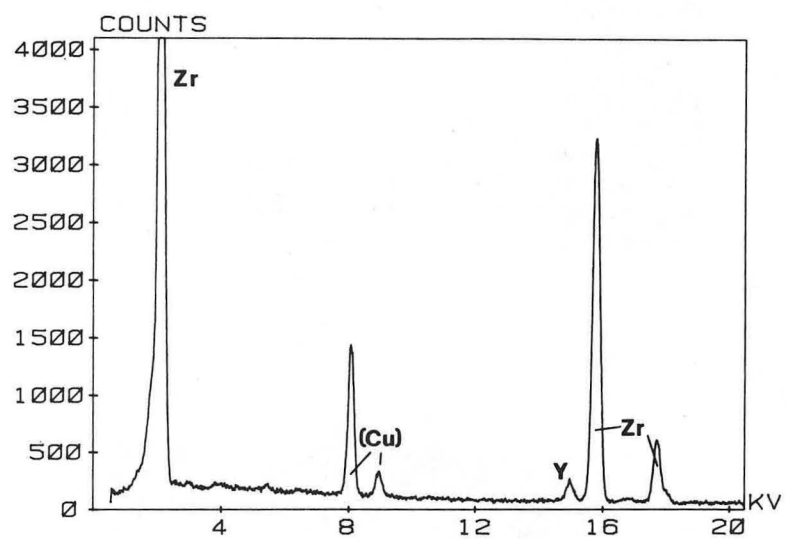


Fig. 11



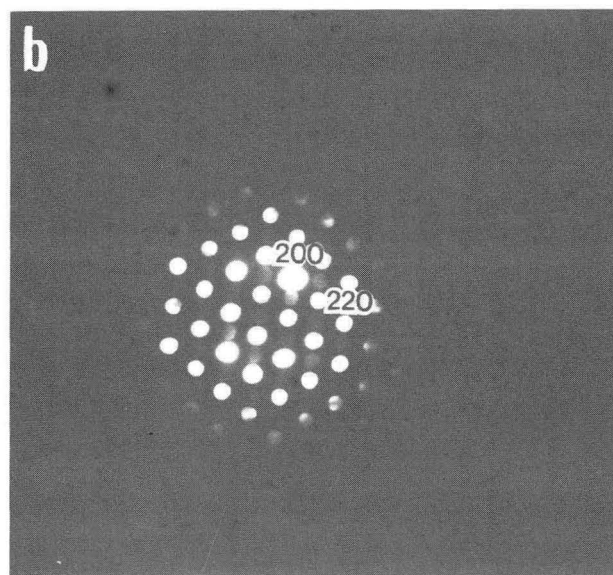
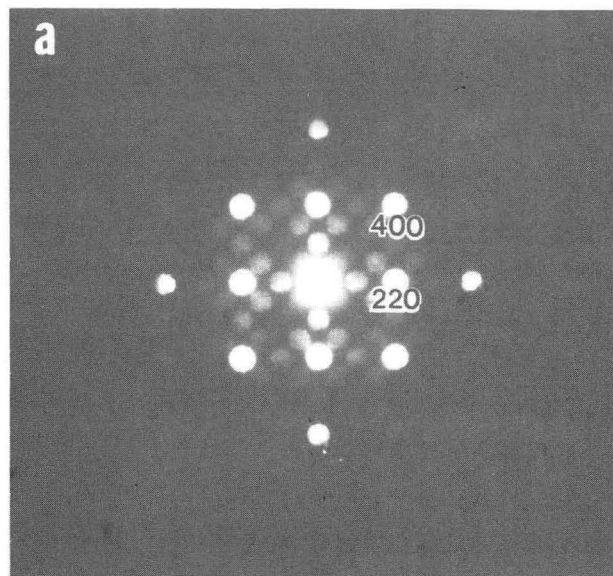
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Fig. 12



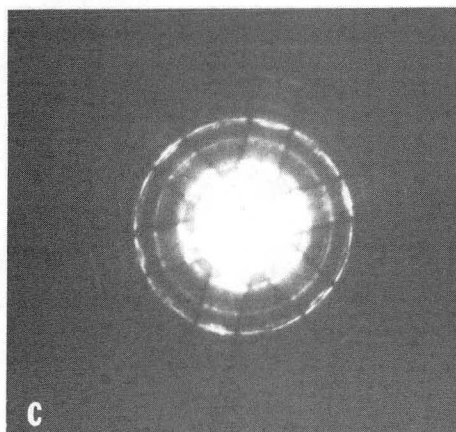
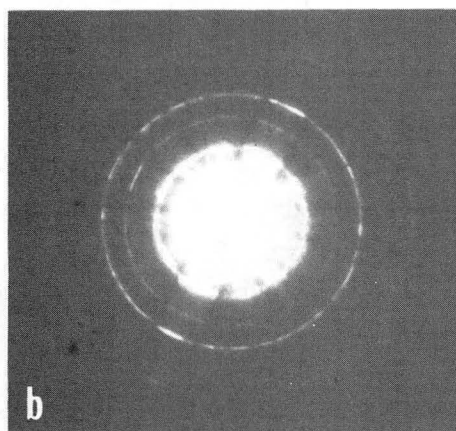
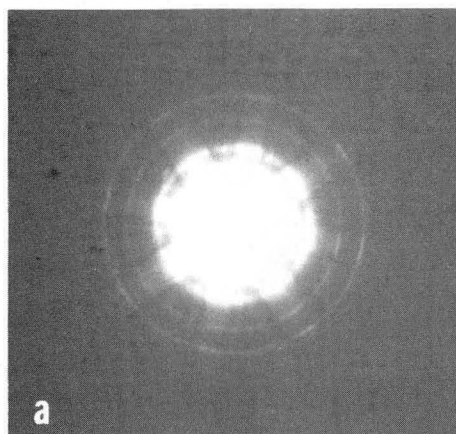
XBL 858-3310

Fig. 13



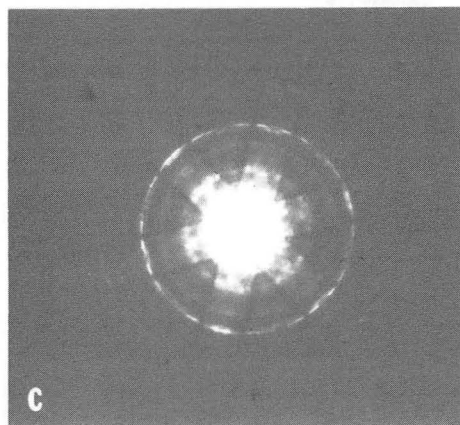
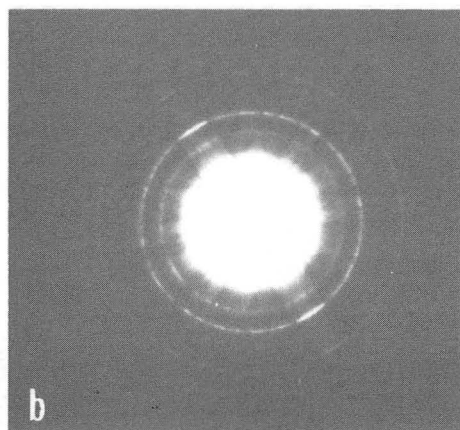
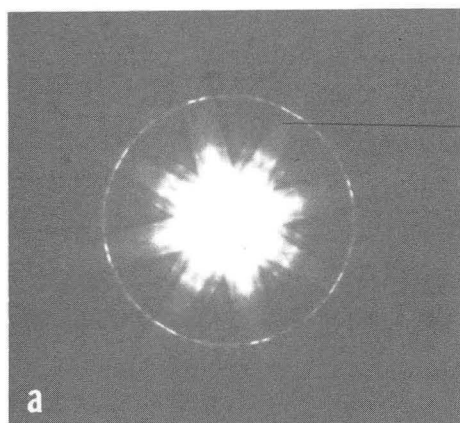
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Fig. 14



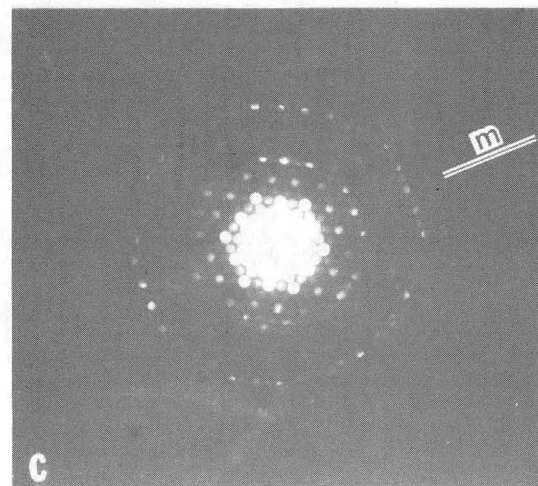
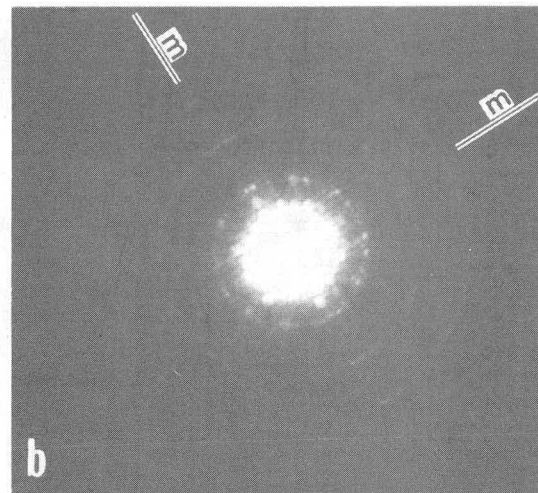
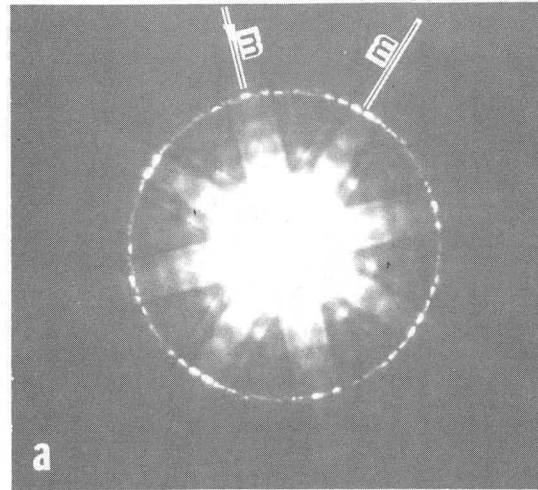
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Fig. 15



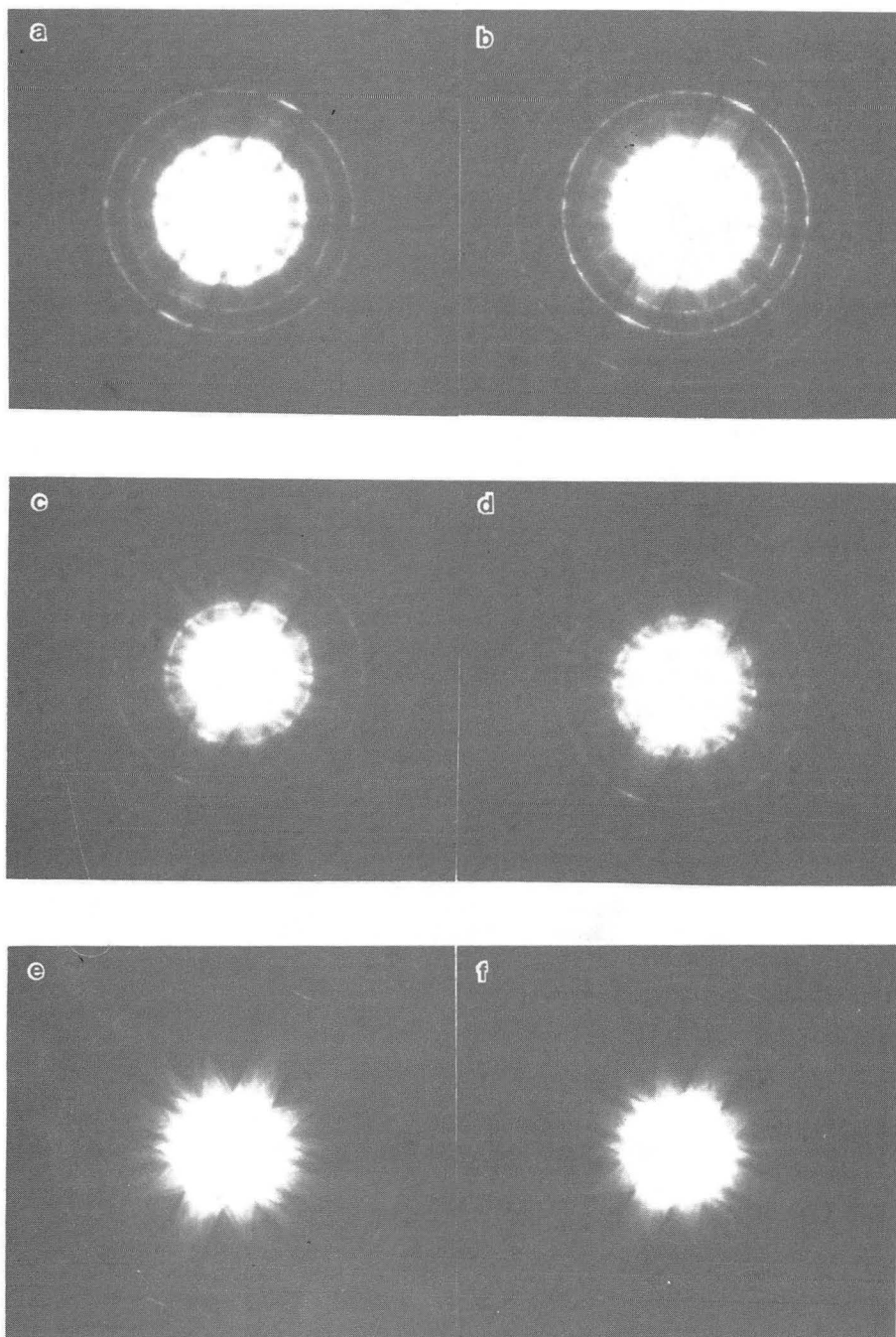
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Fig. 16



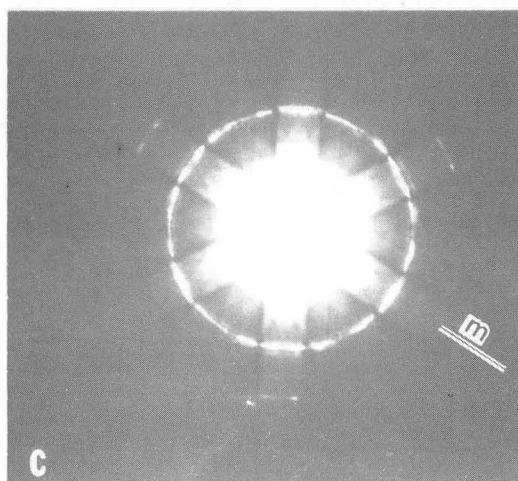
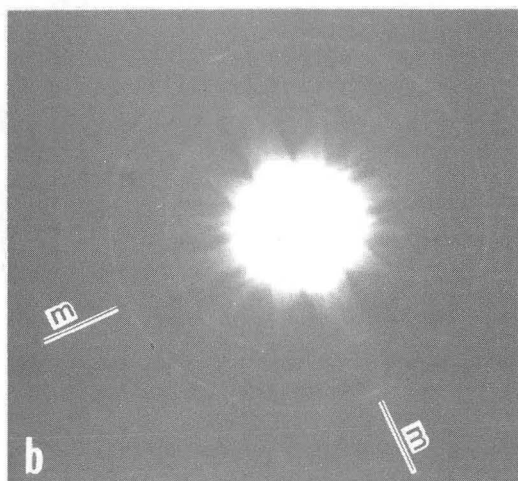
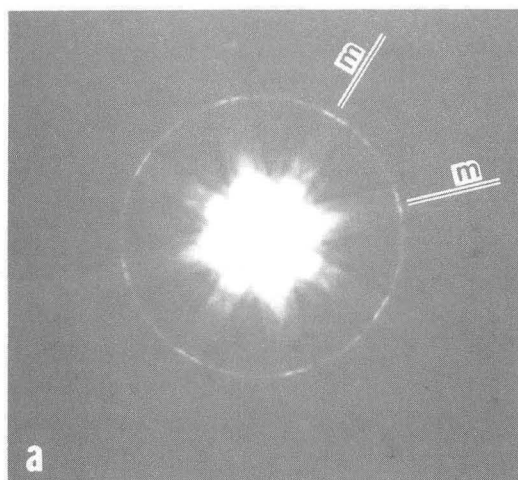
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Fig. 17



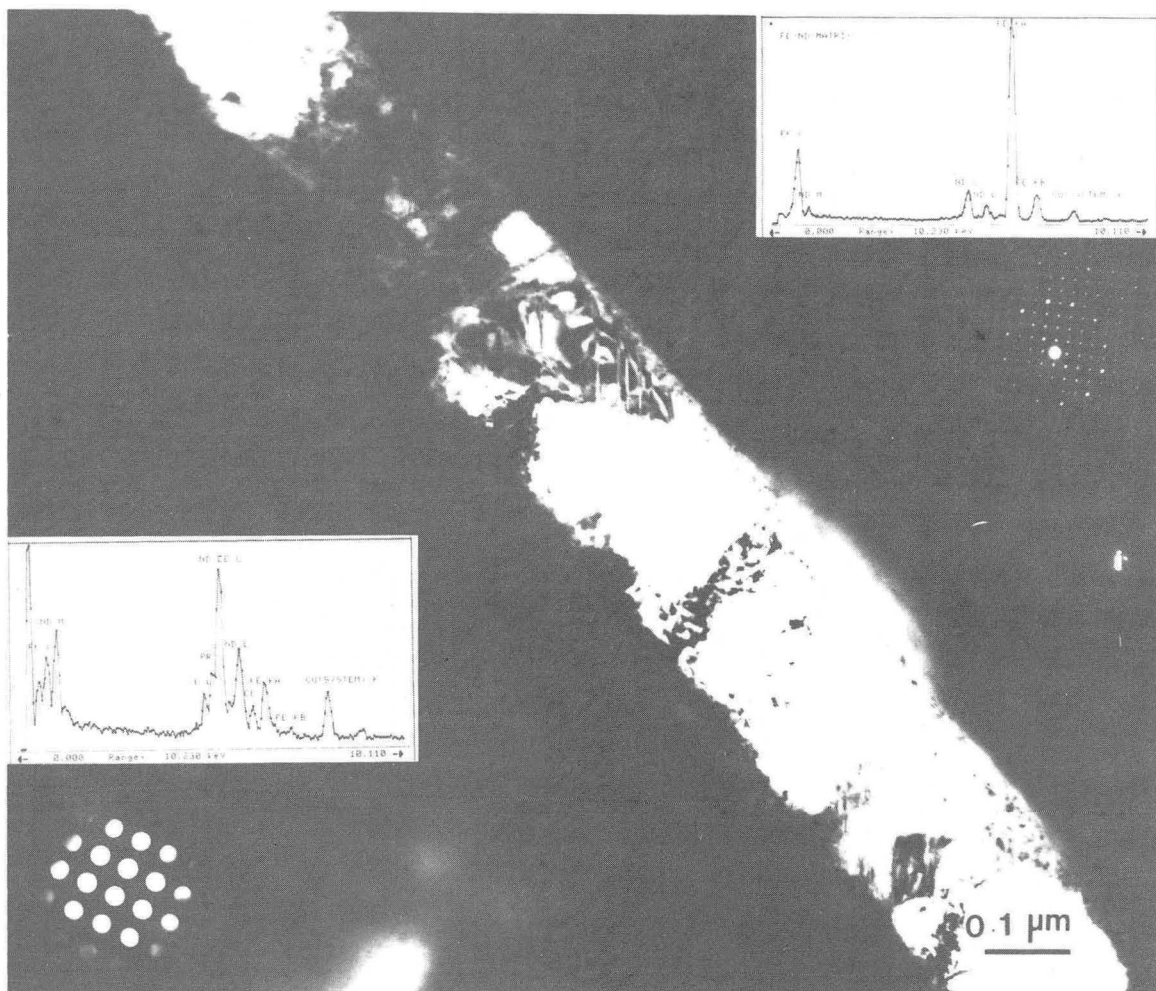
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Fig. 18



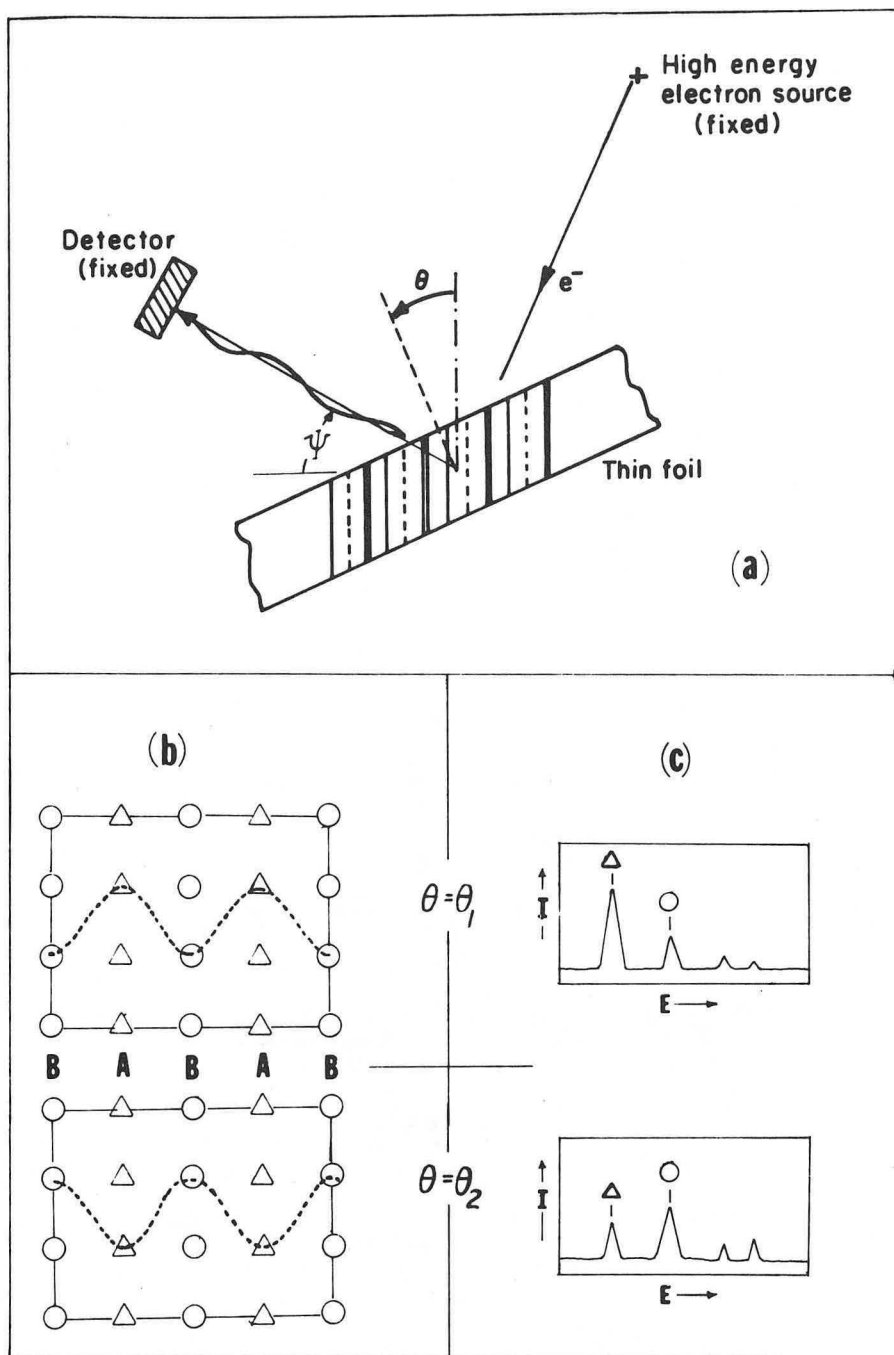
XBB 857-5719

Fig. 19



XBB 853-2444A

Fig. 20



XBL 841-16

Fig. 21

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