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SOME APPLICATIONS OF HIGH VOLTAGE ELECTRON MICROSCOPY TO INORGANIC MATERIALS

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This paper abstracts briefly some of the research programs currently being carried out using the 650 kV Hitachi electron microscope at Berkeley. Many of the programs are interdisciplinary in nature, and involve projects in biology, natural sciences and engineering. The biological work is described in Dr. Glaeser's paper. An extensive review of our main research programs was presented by Bell and Thomas (1971) and a recent summary was given at the Erice School (Thomas 1973). In the present paper some examples of current work on contrast, resolution and applications in ceramics and minerals will be outlined.

One of the main advantages of HVEM for crystals is increased penetration and resolution. Thomas and Lacaze (1973) indicated that except for light elements, the penetration does not improve much beyond 1 MeV, e.g. Si, 9-14μ from 1-2.5 MeV, but no gain was detected for stainless steel. Thus apart from studies of knock-on radiation damage and organic (biological) materials, 1 MeV appears to be optimum for research in inorganic materials.

Examples of Current Research Programs

a) Resolution and Contrast (L.J. Chen) - We have shown earlier the advantages of bright field and dark field techniques utilizing high order systematic reflections for improving resolution e.g. Bell and Thomas (1971) and Goringe et al. (1972). Further work using 13 beam systematic computations and experimental observations on several systems have provided some new results at 650 kV as shown by the corresponding Figs. 1a-d. Figs. 1c,d resolve partials of about 75Å spacing of the pure edge components of a shear loop (b=a/2[011]) in B-doped Si. This spacing is identical to that reported for 100 KV weak beam analysis by Ray and Cockayne (1970) for pure Si. Thus the stacking fault energy in the B-doped specimen is also ~55ergs/cm². The experimental result, Fig. 1c, shows higher contrast of the weak beam images at high voltages (compare to calculation of Fig. 1a).
For resolving closely spaced dipoles the best conditions for imaging have been shown by calculation (9 beam systematic) and experiment to be near 2g (outside contrast) in bright field or the corresponding weak beam d.f. in -lg. These conditions provide maximum image separation, best contrast, and only slightly wider images than if n>2.

Bell (1970) first showed that bright field images in 2g of stacking faults were contrasty or not depending on the sign of the phase change $\alpha = 2\pi g_1 \cdot \mathbf{R}$ at the boundary ($g_1$ is the first order of the systematic set). Subsequently, many more calculations and images have been examined for faults in Si which showed this effect depends on thickness (B.F. Fig. 2) and w. However, the dark field image in g when 2g is satisfied (or slightly negative but not positive) is directly indicative of the sign of a independently of thickness (Figs. 2,3) being of better contrast when $\alpha = -2\pi/3$ (modulus 2\pi). Thus, this D.F. image gives a rapid method for determining whether faults are intrinsic or extrinsic, especially for loops etc. within the foil.

b) Ceramics (O. van der Biest - lithium ferrite) Above 750°C lithium ferrite (LiFe$_5$O$_8$) has an inverted spinel-structure, i.e. with Fe$^{3+}$ on tetrahedrally coordinated sites and a 3:1 mixture of Fe$^{3+}$ and Li$^+$ on the octahedral sites. The latter take on an ordered arrangement below 750°C. The ordered structure contains anti-phase boundaries (APB), with a displacement-vector of 1/2<110> and an example is shown in Fig. 4. The fringes are due to a small angle boundary. Fig. 5 shows an example of {110} cation faults. Applications of contrast criteria showed that the faults can be characterized by a displacement vector $\mathbf{R} = 1/4<110>$, with $\mathbf{R}$ always perpendicular to the fault plane. These faults are thus growth faults. As 1/4<110> is a lattice vector for the oxygen sublattice, the displacement affects only the cations. For spinel reflections, the faults have all the properties of π faults.

Figs. 6a,b,c show contrast conditions for APBs (a), {101} faults (b), and 1/4{101} partials (c). Weak π contrast occurs in 6(b) due to the influence of the
superlattice reflections in the systematic set. This effect can cause difficulties in contrast identification at high voltages. Fig. 6(c) shows the further advantage discussed in Sec. 2 of high resolution imaging in ng (n=6) in which the two partials bounding the (101) fault are well resolved. Examples of {111} faulting associated with a/6<111> displacements have also been resolved.

c) Minerals - Several investigations of transformations and deformation of minerals (e.g. enstatite, feldspars) have been carried out. Here we have space only to summarize the main conclusions concerning the ordered structures of anorthites (calcic plagioclases, Muller et al. (1973). Two different types of APBs have been resolved, viz. type b APBs (b reflections h+k odd, l odd) and type c APBs (c reflections h+k even, l odd). The displacement vector of b-APBs was determined as 1/2[110]. i.e., the formation of b-APBs is connected with Si-Al ordering; Christie et al., (1971). The anti-phase vector of c-APBs was found to be 1/2[111].

Mineralogy-Processing - Because of the increasing concern over sources of raw materials, considerable interest exists in searching for metal producing ores on the ocean floors e.g. the Pacific Ocean bed is estimated to contain at least 10^11 tons of manganese nodules, containing Ni, Fe, Cu etc. e.g., Mero (1965).

Because of the higher resolution in diffraction, and greater penetration the high voltage electron microscope is useful not only in mineral identification of particles which are too small for x-ray analysis, but also for characterizing particle morphology (important in extractive metallurgy). Details of the present research program will be published elsewhere (von Heimendahl et al. 1973), but one of the main conclusions was that ferric hydroxide is the main iron mineral in the nodules examined. Fig. 7 shows an example of particles in the range 100-450Å. Identification is carried out with the aid of computer programs, which are also used in environmental research e.g. analysis of asbestos fibers which are too thick (=2μ) for identification at 100 kV (e.g. Thomas 1970).
Fig. 1a, b--Resolution of partials; depth $2.5 \xi g = 6 \xi g/\xi g = 0.06$.  
1c, d--Corresponding example.
Fig. 2. Computer simulated images of stacking faults in silicon.
Determination of the sign of $\alpha$ from a dark-field of $g$, when $W_{2g} = 0$. 

Fig. 3.
Fig. 4. LiFe$_5$O$_8$ quenched from 950°C aged 16 min. 650°C [111] foil; Bright field image 650 kV.
Fig. 5. Disordered LiFe$_{5}$O$_{8}$ showing \{110\} cation faults.
Fig. 6. Contrast examples showing defects in fully ordered LiFe$_2$O$_4$. (a) 011 superlattice reflection (b) 0.022 spinel reflection cation fault visible (c) 066 spinel reflection-partials resolved.
Fig. 7. (a) Bright field and (b), (c) dark field images of Mn nodule showing 100-540Å particles of Fe(OH)$_3$ identified from rings indicated by doubly exposed image of objective aperture superimposed, nodule from 1270 meters.
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