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Channelling Enhanced Microanalysis: A High Resolution Analytical Technique for Atomic Site and Species Determination

K.M. Krishnan

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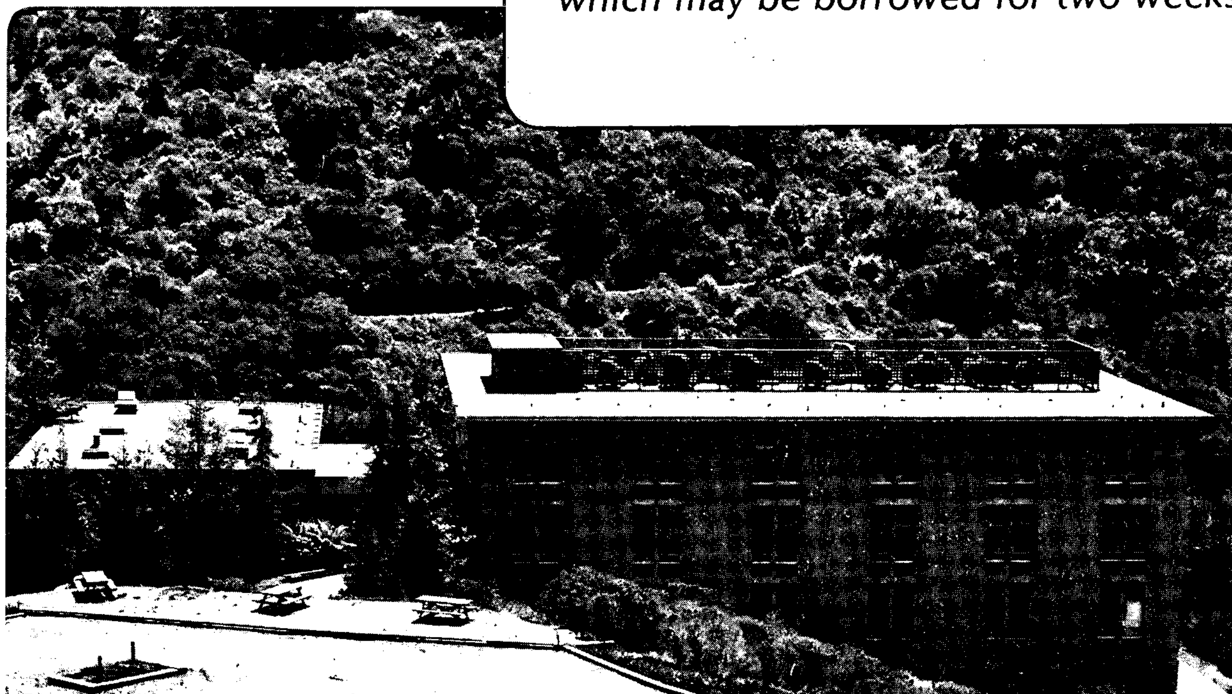

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CHANNELLING ENHANCED MICROANALYSIS: A HIGH RESOLUTION ANALYTICAL TECHNIQUE FOR ATOMIC SITE AND SPECIES DETERMINATION

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ABSTRACT

The formulation, development and applications of a novel crystallographic technique to determine specific-site occupations of elemental additions in crystalline materials, using the channelling or Borrman effect in electron diffraction, is reviewed. This technique is based on the effect of incident beam orientations on the intensities of either the characteristic x-ray emissions or the characteristic electron energy-loss edges. The formulation of the technique under both planar and axial channelling conditions for crystalline materials is presented. In general, this technique can distinguish neighbours in the periodic table; involves no adjustable parameters, external standards or special specimen preparations; is applicable to trace elemental concentrations (0.2-0.3 wt % or 10^{25} atoms/m^3); is very accurate and can be applied routinely at high spatial resolutions (~10-40nm). In the EELS formulation the technique can also provide specific site valence information. Finally, applications of this technique to site-occupation studies in a variety of materials is outlined.

1. INTRODUCTION

The interaction of a highly monoenergetic beam of fast electrons with a thin film sample produces a wide variety of primary and secondary physical phenomena. In electron energy loss spectroscopy (EELS), the primary process of electron excitation, defined by the fast electron losing a characteristic amount of energy, is studied. Of the wide variety of secondary or deexcitation processes, the characteristic x-ray emissions monitored either by solid state detectors (Energy Dispersive X-ray Spectroscopy) or detection crystals (Wavelength Dispersive X-ray Spectroscopy) find wide application in microstructural characterization. While EELS provides information related to the bonding and electronic structure of the material, a principal application of both these spectroscopies is in the area of microanalysis, where the characteristic x-ray peak and electron energy-loss edge intensities are interpreted in terms of the composition of the sample.

However, it has been observed that these electron-induced characteristic x-ray emissions are also dependent on the orientation of the incident beam (Figure 1). A comprehensive theoretical formalism to describe this phenomenon, with particular emphasis on its influence on microanalysis, was originally proposed by Cherns, Howie and Jacobs [1]. In general for crystalline materials, an incident plane-wave of electrons under conditions of strong dynamical scattering sets up a standing wave within the crystal. The intensity modulations of this standing wave within the crystal unit cell are a function of the incident beam orientation. For certain incident orientations, the standing wave maxima are coincident on atomic sites and are accompanied by both enhanced absorption of the primary beam as well as an increase in the characteristic x-ray emissions--a process that is highly localized at the atomic sites. This orientation dependence of the emission product (EDXS) as well as the energy-loss electrons in transmission (EELS), has been developed into a powerful crystallographic technique for specific site occupancy or valence determinations called ALCHEMI or atom location by channelling-enhanced microanalysis [2-6]. In the case of EELS, the experimental arrangements are more flexible, as both the incident and collection direction are selected independently, and the channeling and blocking effects are incorporated in the analysis [7].

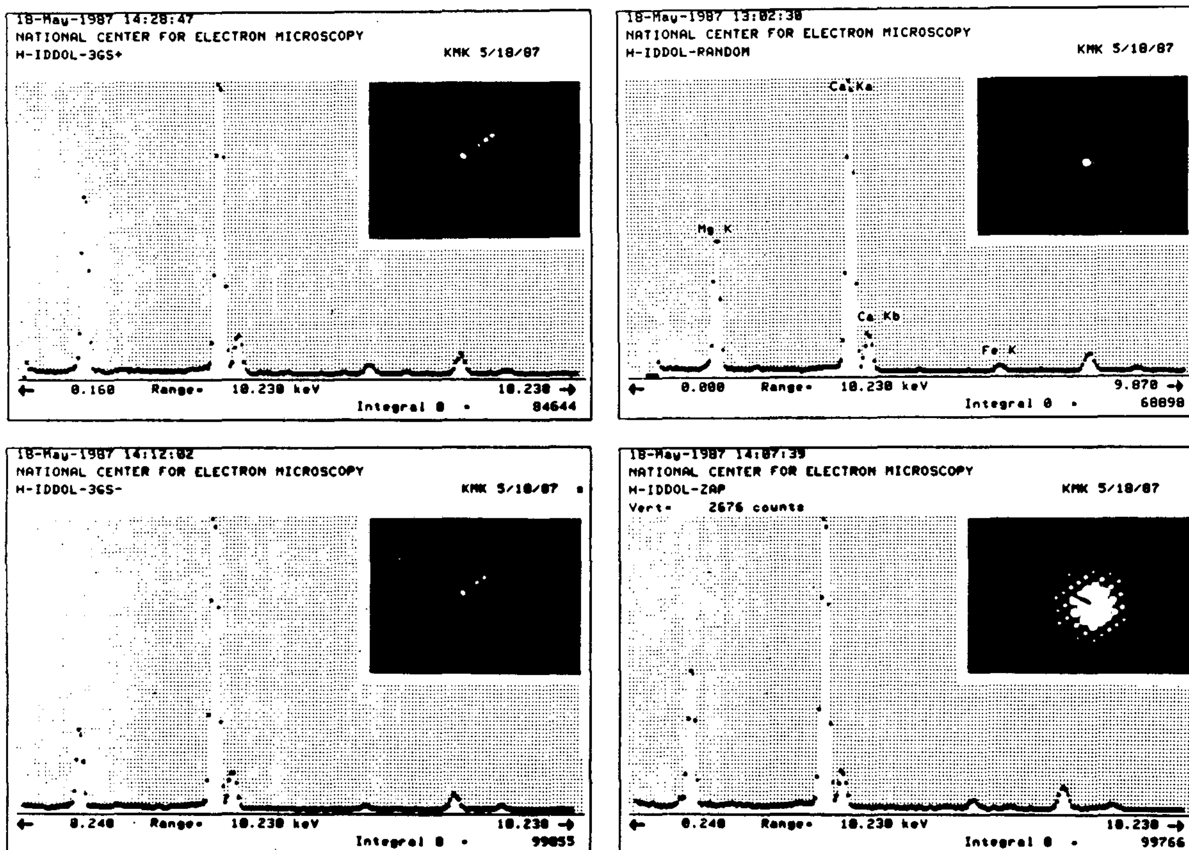

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Fig. 1. A typical example of the dependence of characteristic x-ray emissions on the incidentd electron beam orientation. To avoid these channelling effects in routine microanalysis, the specimen should be tilted to an orientation in which no lower order diffraction vectors are excited (top right). For the dolomite structure (Fig. 3b), the best planar channelling conditions are when a [0001] systematic row is excited and at orientations corresponding to either small positive (top left, when an enhancement of Mg Kα is observed) or negative (bottom left, when an enhancement of the Ca Kα is observed) excitation errors of the third order (3g) Bragg diffraction condition. It can be seen that the impurity Fe Kα intensity follows that of Mg Kα, showing similar site occupancy.

2. PHYSICAL DESCRIPTION OF THE TECHNIQUE

A typical experimental arrangement for the characteristic x-ray emission case in a conventional TEM, in the planar channelling geometry is shown in Figure 2a. The take-off angle(ψ) varies from 20° to 70° depending on the position of the EDXS detector for that specific instrument. However, the higher the take-off angle, the easier it is to do the measurements as the specimen need not be tilted to a specific orientation for optimal x-ray detection. The projected crystal structure with the standing-wave pattern of the primary beam, set up as a result of the strong dynamical scattering, is shown in Figure 2b. For a systematic or planar channelling condition, the wavefield of the incident electron in the crystal is two-dimensional (i.e. constant in a direction normal to the page). The modulation of the standing wave on specific crystallographic planes is then a function of the incident-beam orientation. Highly localized secondary phenomena such as characteristic x-ray emissions are also a function of these modulations of the primary beam (Figure 2c). For a particular favourable orientation (θ_1), the Bloch waves are maximized on the A planes with a concomitant increase for the elements occupying the sites Δ. For the other favourable orientation, the maximization is on the B planes with a corresponding increase for the elements occupying the sites 0.

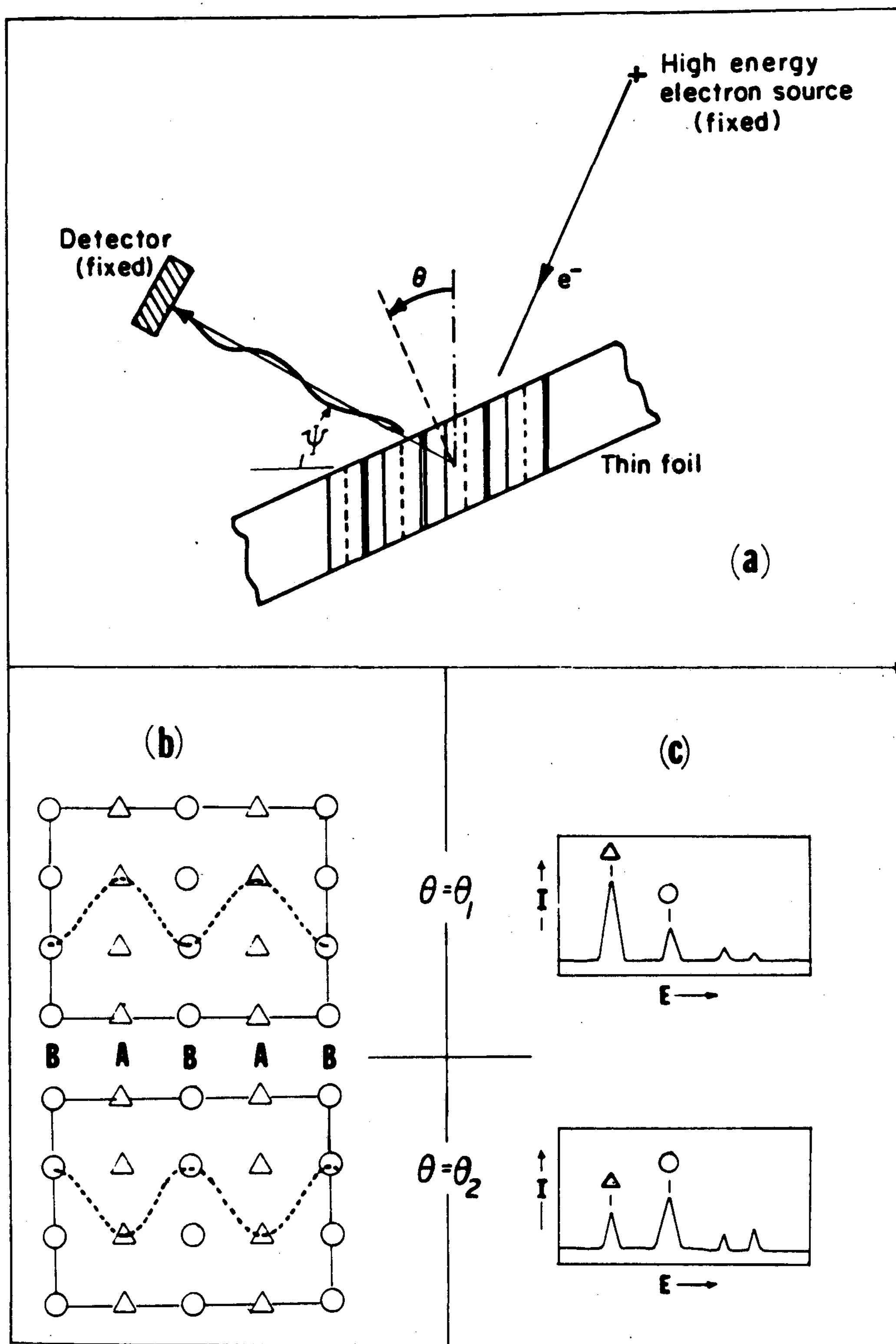

Fig. 2. Physical principles of Channelling Enhanced Microanalysis.

The development of a meaningful technique of quantitative site occupancy determinations, utilizing the above variations of the x-ray intensities with orientation, is then largely dependent on both the ability to determine these favourable orientations and to obtain an independent measure of the electron intensity modulations over the unit cell. For electrons accelerated through kilovolt potentials, the latter can be calculated using a dynamical many-beam theory [8,9]. However, the need for a theoretical prediction of the electron wave field in the crystal can be avoided by using the x-ray emission from a reference atom whose distribution in the host crystal lattice is known [3]. Further, as secondary emission processes are highly localized, these intensities are then proportional to the thickness-averaged electron intensity on specific atomic columns.

For a planar channelling or systematic orientation (a single row of spots are seen in the diffraction pattern) the crystal potential is averaged in two orthogonal directions normal to the excited systematic row. For the simplest case, a crystal with a layered structure, the appropriate systematic orientations can be determined by mere inspection [4]. For example, the spinel structure compounds (Figure 3a) can be resolved in the [001] projection into alternating (400) planes of tetrahedral (Mg) and octahedral (Al) sites and hence a g = 400 systematic row at the second order Bragg diffraction condition can be easily seen to be appropriate for this kind of experiment. Alternatively, for the dolomite structure (Figure 3b), the candidate sites (Mg and Ca) occupy alternating planes at one third the unit cell parameter along the c-axis. Hence by inspection, it can be concluded that a g = 0001 systematic row at the third order Bragg diffraction condition (Figure 1) would give the best planar channelling results.

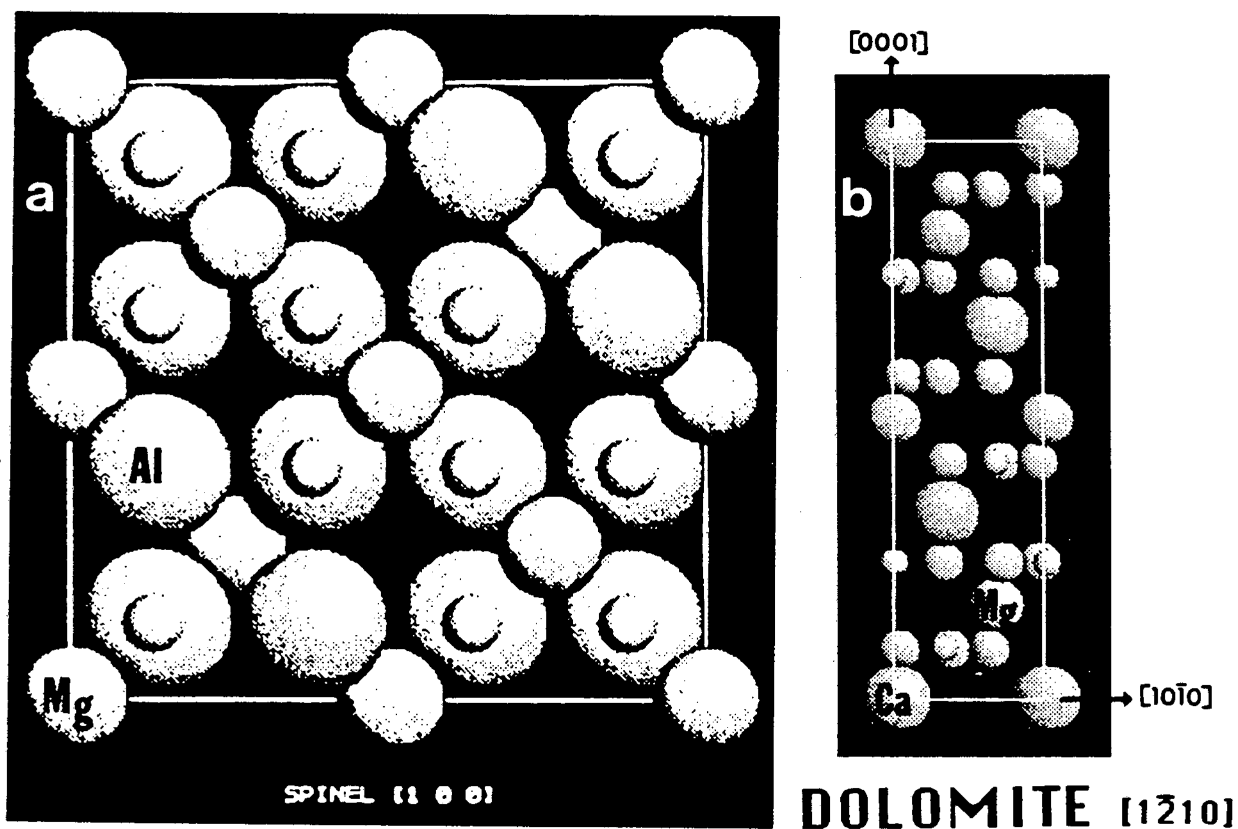

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Fig. 3. (a) The spinel structure in the [100] orientation. Notice that this structure is layered, i.e. in this crystallographic projection, it can be resolved into alternating layers of parallel non-identical planes [A,B,A,B ...] each plane containing one or more specific cyrstallographic sites. (b) The dolomite structure in the [1210] orientation. The c-axis has been exaggerated for clarity. A [0001] systematic row at the third order Bragg diffraction condition is best for planar channelling. This can be inferred by inspecting the unit cell and noting that the candidate sites (Mg or Ca) occupy positions on planes at one third the lattice parameter in the c-direction. These figures were generated using the CEMPAS [35] image simulation programs at the NCEM.

Now, if an *a priori* knowledge of the distribution of some reference elements in the host lattice is available, their characteristic x-ray intensities could be used to obtain a measurement of the thickness-averaged electron wavefield intensity on specific atomic planes. In the simplest case [3], the distribution of impurity or alloying additions is determined by an elegant method of ratios of their characteristic x-ray intensities with respect to those of the reference elements at two different orientations; i.e. at a channelling orientation and at a random non-channelling orientation defined such that no lower order diffraction vectors are excited. For a crystal such as the spinel, $MgAl_2O_4$ (Figure 3a) consisting of two reference elements (Mg [a] on tetrahedral sites and Al [b] on octahedral sites), elements a,b lying exclusively on planes A, B respectively, the fraction of the unknown dopant (Fe, say) lying substitutionally on plane B, C_x is given by [3,10]

$$C_x = \frac{\dfrac{N_x^1}{N_x} - \dfrac{N_a^1}{N_a}}{\dfrac{N_b^1}{N_b} - \dfrac{N_a^1}{N_a}}$$

where the Ns are observed x-ray intensities for the elements a, b, x at the random orientations and the N^1s are the intensities for the same elements at the channelling condition.

If the structure is layered, but the requirement of the existence of at least one species that lies exclusively on one of the alternating planes is violated, more than one orientation along the same systematic row will be necessary to perform the analysis. The precise number of orientations required will then be determined by the stoichiometry of the original compound and the actual distribution of the reference elements before alloying [11,12].

In the general case, where a projection of the crystal structure that separates the candidate sites into two planes each with a specific internal reference element cannot be found (for example the garnet structure, $I4_1/a32/d$), the appropriate planar-channelling conditions cannot be determined by inspection nor can the characteristic x-ray intensities be used as a measure of the thickness averaged electron intensity for any specific site. Then the characteristic x-ray emissions have to be calculated and the experimental intensities refined using a constrained least-squares method to determine the occupancies [5].

In conclusion, each problem of site occupancy to be solved in the planar channelling orientation has to be tackled separately, beginning by classifying the crystal structure into one of the three categories described above, and then proceeding with the appropriate formulation [4].

Electron channelling in the axial geometry represents a useful alternative to the experimental arrangement discussed thus far [6,13]. An electron beam incident close to the zone axis excites several low-index Bragg diffraction vectors, thus setting up several simultaneous standing waves [14]. For exact zone-axis orientations, this results in the electron beam being effectively channelled into columns with the current being maximized on atomic strings [15] and with an accompanied increase in the characteristic x-ray emissions. Further, the channelling effects are considerably enhanced in the axial case [15,13]. This geometry is particularly suited for studying the degree of substitution of small quantities of dopants in a monatomic crystal. An example of such an application is shown in Figure 4. The details of analysis, which are essentially the same as that for the planar channelling are given elsewhere [6].

In terms of practical applications, the axial geometry gives a stronger effect but generally it is difficult to find axial orientations which separate nonequivalent sites of the unit cell into distinct columns each containing a specific reference atom. On the other hand, finding planar orientations which separate candidate sites onto separate planes with specific reference elements is relatively straightforward for most crystal structures. Further, the planar method has demonstrated wide applicability in a variety of applications ranging from impurity site occupancy determinations in complex sublattices to specific site valence studies using EELS.

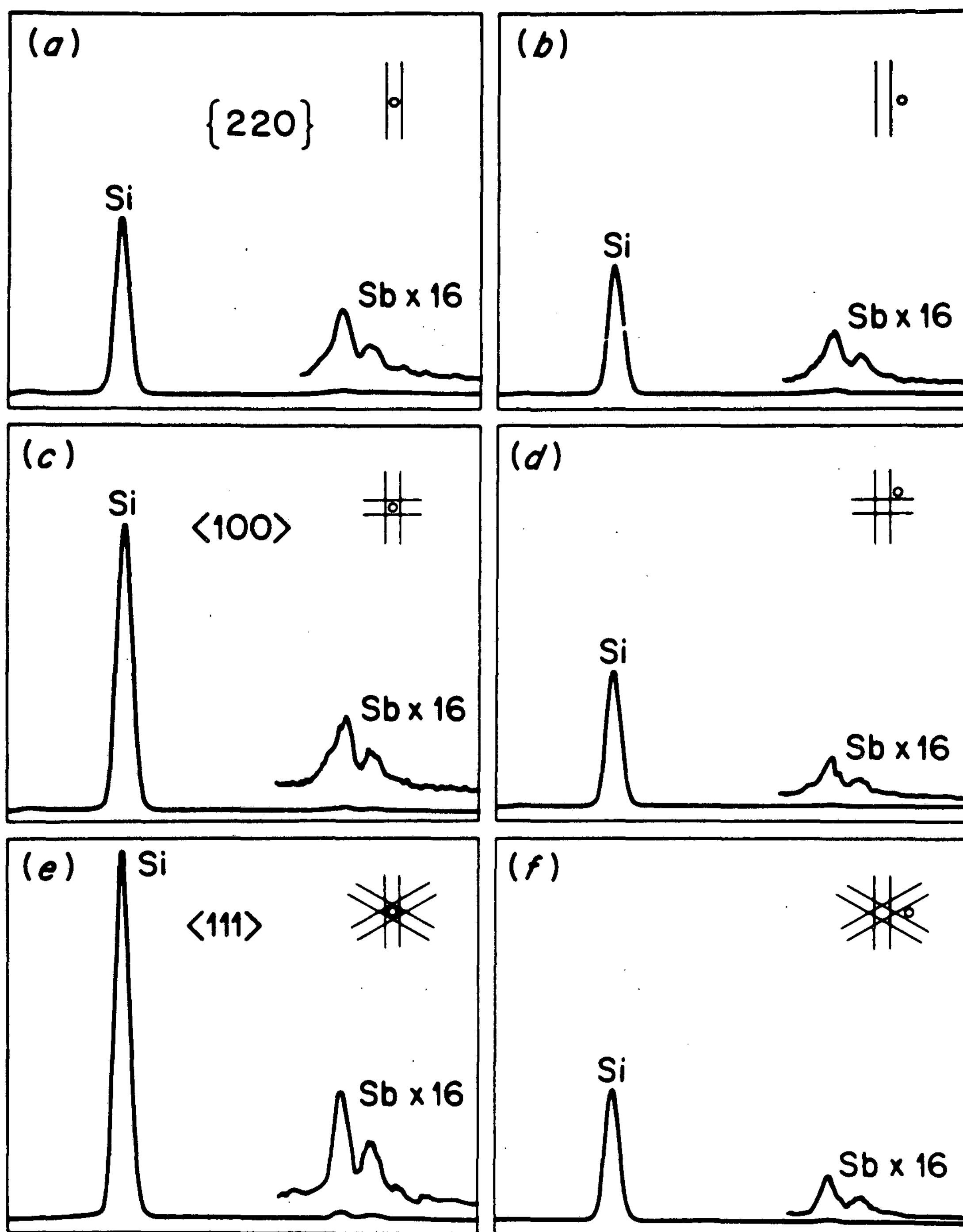

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Fig. 4. A comparison of axial and planar channelling for Sb dopants in monatomic silicon. For all three zone axis conditions an enhanced effect is observed in the axial orientation. Further, the fraction of substitutional dopant can be quantitatively determined using a simple analysis, provided corrections are made for the strong delocalization effects observed in axial channelling [6,15]

Characteristic x-ray emissions and the corresponding energy-loss edges should, in principle, show identical variation with the incident beam orientation. However, within the single scattering regime, applying the principle of reciprocity, it can be shown that the intensity in EELS for different site occupations can be effectively squared by choosing the position of the detection aperture and placing it at an appropriate part of the diffraction pattern to be energy analyzed [16].

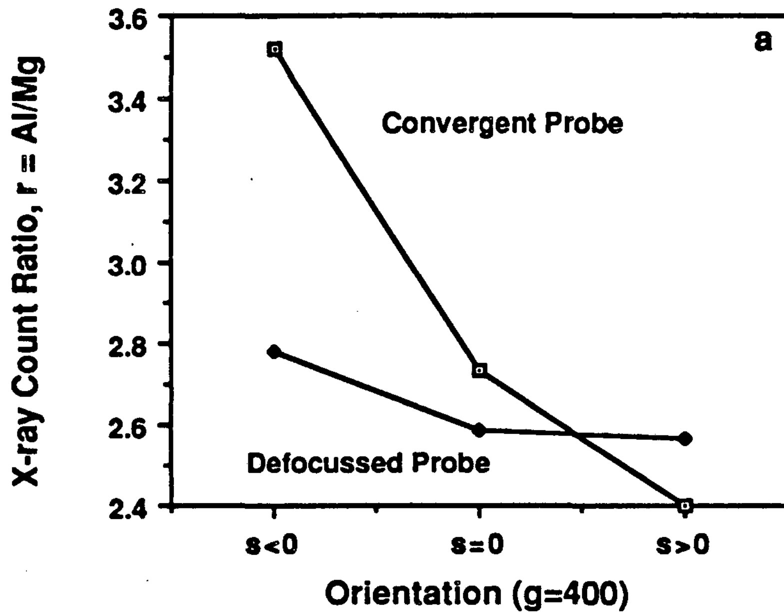
3. DISCUSSION

3.1. Experimental Considerations. These site-occupancy measurements can be routinely carried out on most commercial electron microscopes equipped with either an energy dispersive x-ray detector or an electron energy-loss spectrometer. The methods are, of course, subject to all the limitations of the two individual spectroscopic methods. Moreover, no special specimen preparation methods are required. However, since all intensities are thickness-averaged, the distribution of impurities in the crystal should be uniform with depth. Any bending or thickness changes under the probe are unimportant as both the impurity as well as the reference elements are affected the same way by any local change in orientation.

3.2. Localization Effects. A basic assumption in performing these channelling experiments is that the inner-shell excitations concerned are highly localized at the atomic centers [3,5]. This localization is a function of the amplitude of thermal motion as well as the impact parameters ⟨b⟩, defined as the expectation value of the distance at which a fast electron can transfer a specified quantity of energy to the core-electron. It had been estimated that for characteristic x-ray emissions of energy greater than 1keV, thermal vibrations provide the predominant influence on localization at room temperature [17]. However, recent calculations on localizations [18] based on a fully dynamical 49–beam (e,2e) model for ionization, for the ⟨111⟩ zone-axis orientation in GaAs, indicate that differences do occur for characteristic x-ray emissions in the 1-10keV range. Similar localization effects have been obseved for Cr-Kα (5.4keV) in garnets [13] and for Sb/As in Si [15], both in the axial geometry. However, it is expected that the delocalization problem is more pronounced in the axial compared to the planar channelling case. This is because when many reflections are excited, contributions from Fourier components with large g vectors tend to delocalize the wavefield of the fast electron. In most cases, experimental correction factors (c-factor) for localization can be determined with relative ease. These c-factors are the ratios of the channelling effect for the higher energy Kα to the lower energy Lα lines [6].

Performing these channelling experiments at low temperatures has some significant advantages [19]--the scattering potential is less attenuated in higher order g-vectors leading to a greater variation in the electron beam intensities on the different sites and the amplitude of thermal vibration is considerably reduced. The latter is material dependent and no improvement is expected if the mean free path for phonon excitation becomes appreciably larger than the specimen thickness. For enegy-loss experiments, it can be shown by a simple application of the uncertainty principle that the distance a fast electron can pass from the atom and still ionize it is inversely proportional to the momentum transfer associated with the inelastic scattering event. Simple calculations show [20], that by analyzing electrons scattered over large angles (i.e. large momentum exchange), the sensitivity can be greatly increased even down to 500eV losses as the corresponding inelastic scattering event would be more localized!

3.3. Effect of the helical path. These techniques give best results for a collimated parallel electron beam. However, in most modern TEMs, the specimen is immersed in the magnetic field of the objective lens and the electron follows a helical path in the vicinity of the sample. It has been pointed out [21] that this configuration introduces both a radial as well as a tangential component of parallelism. Further, it has been suggested [22] that the tangential component due to the helical trajectory is the dominant criterion of parallelism and that best results are obtained with a substantial probe convergence compared to a parallel beam, provided that the convergence angle is smaller than the operational Bragg angle. However, a recent experimental investigation [23] has shown that best results are not always obtained for the case of a beam convergent on the specimen surface, even when the convergence angle is smaller than the Bragg angle. In any case, this effect is machine-dependent and a simple experiment [23], taking into consideration all factors for optimal data collection, such as the convergence angle and primary lens excitation combinations, can be performed to obtain the best working conditions (Figure 5).



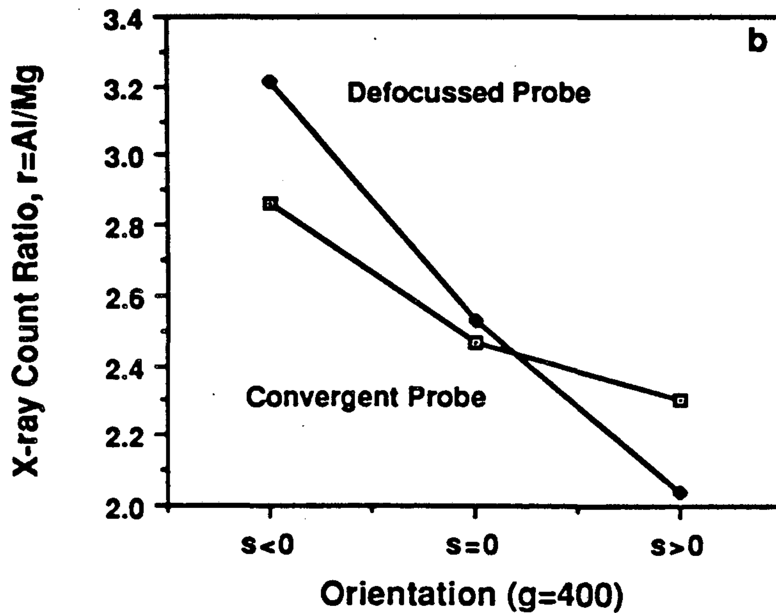


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Fig. 5. Summary of results, comparing the sensitivity of the orientation dependence to the helical path of the electron beam in a typical microscope, for two practical incident probe conditions. A spinel sample was used and a g = 400 systematic row was excited. (a) Small convergence angle (α = 0.8mrad) - better channeling for the incident probe convergent on the specimen surface (note: diffraction disks are obseved); (b) Larger convergence angle (α = 3.5 mrad) - better orientation dependence or channelling for a defocused probe (giving rise to sharp diffraction spots in the back focal plane of the objective postfield).

3.4. Spatial Resolution. The ability to use convergent probes and yet observe these channelling effects (within the constraints discussed above) makes it possible to routinely achieve a spatial resolution of 10-40nm. However, the spatial resolution is also determined by the statistics of the EDX detection process. It is estimated that reasonable results can be obtained using a 20nm probe for a 10^{25} atoms/m^3 distribution of impurities. In order that the dynamical wavefunction be well sampled in depth the following simple criterion has to be satisfied [3]

$$\xi_g \, n \, A \geq 1$$

where ξ_g is the dynamical extinction distance for the reflection g, n is the uniformly distributed concentration and A is the projected area of the electron probe. Finally, the use of a higher brightness source, such as a field emission gun would, in principle, considerably improve the lateral spatial resolution of these techniques.

3.5. Acceleration Voltage. A systematic study has been carried out to study the combined effect of acceleration voltage and incident beam orientation on the characteristic x-ray production in thin crystals [24]. For $MgAl_2O_4$, the orientation dependence undergoes a reversal in character above a particular voltage. This "inversion voltage", also observed experimentally, is in agreement with earlier theoretical predictions [25]. However, this inversion voltage behavior is different from the conventional critical voltage effect [26]. In any case, the experiments should always be performed at the same accelerating voltage to obtain best results.

3.6. Effect on Microanalysis. It must be intuitively obvious that these channelling effects could play a detrimental role in conventional microanalysis using either EDXS or EELS for polycrystalline samples. In most practical cases, it should be possible to eliminate any errors due to channelling either by systematically tilting the sample to an orientation such that no lower order diffraction vectors are excited (Figure 1) or by using a large illumination aperture such that the use of a large convergence angle effectively averages over a wide range of incident beam orientations. Should these be impossible, it is quite feasible [1] to compute the necessary correction which may arise because of the orientation effect.

4. APPLICATIONS OF CHANNELLING ENHANCED MICROANALYSIS.

The techniques of channelling enhanced microanalysis or ALCHEMI, are not only well established but have found wide application in microstructural characterization. Representative examples of current applications in a wide variety of materials, are given in Table 1. These applications can be broadly summarized as follows:

4.1. Specific site occupancy determinations. Indeed this is the most widespread application of this technique. Following a careful inspection of the crystal structure, with particular attention to the distribution of the candidate sites in the unit cells, the choice of the experimental arrangement (axial or planar channelling) can be made. For specific site occupancy studies, it is generally simpler to monitor the characteristic x-ray emissions, provided the localization corrections are incorporated if and when they are required. With this approach, impurity site occupancies for almost any crystal structure can be routinely determined.

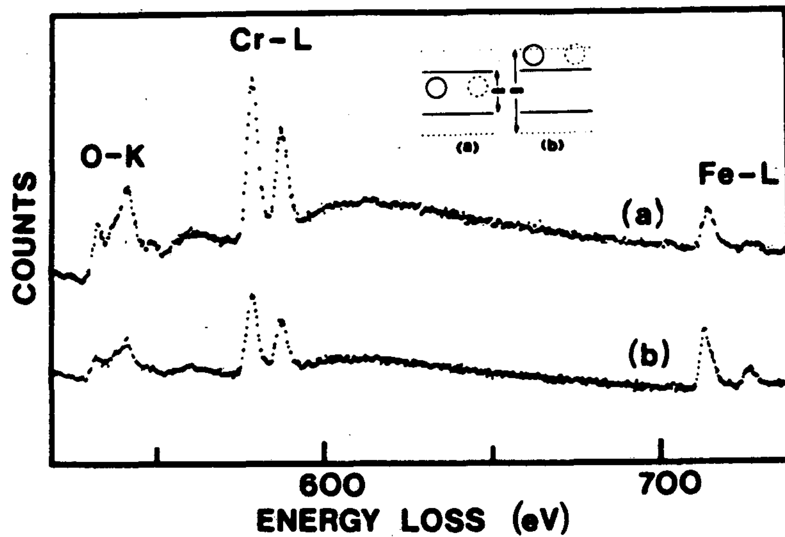
Site occupancies determined by ALCHEMI have been compared with both x-ray and neutron diffraction with excellent results [26]. These channelling techniques are capable of resolving adjacent elements in the periodic table and site occupancies of trace element compositions can be resolved. The errors in these determinations can be in the range of 3-10% depending on which formulation is used. As described earlier, this high resolution technique requires no adjustable parameters unlike EXAFS/EXELFS and high resolution electron microscopy. A general discussion of the experimental impediments to ALCHEMI and sugggestions to overcome them are given elsewhere [4].

TABLE 1

REPRESENTATIVE APPLICATIONS IN MATERIALS CHARACTERIZATION

Material	Comments
Semiconductors	
Si	Dopant (Sb,As) distribution, x-ray emissions, axial geometry [6,15]
InGaAs	Determination of atomic displacements, planar geometry [28]
InP,GaAs	Temperature dependence [19]
GaAs	Role of point/line defects in the degradation of light emitting diodes [29]
Magnetic Materials	
$Sm_2(Co,TM)_{17}$	Effect of dopant (Fe,Mn) site occupancy on coercivity, planar channelling, EDXS [12].
$(Y,RE)_3Fe_5O_{12}$	Role of rare-earth additions (Sm,Lu) on the uniaxial anisotropy of epitaxially grown garnet films [30]
Ceramics	
$BaTiO_3$	Ca impurity site occupancy in a ceramic capacitor, planar channelling [31]
$CaTiO_3$	Nuclear-waste material [32]
Alloys	
Nb_3Sn	Superconductor alloy, upper critical magnetic field, systematic row [33]
Ti_3Al	Super alloys, Nb additions [34]
Minerals	
Feldspars	Comparison with x-ray and neutron data, planar channelling [36]
Spinels	Chromite spinels, EELS, specific site valence studies [37].

4.2. Specific Site Valence Studies. Because of the superior energy resolution for EELS (1-2eV using conventional LaB_6 filaments) when compared with EDXS (~ 150eV for 5.9 kV x-rays) it is possible to detect changes in oxidation states by the small chemical shifts observed in the EELS core edge features. For example a 2eV chemical shift is observed between Fe^{2+} and Fe^{3+} states. Combining this chemical shift with the selective enhancement of the different candidate sites, by the appropriate choice of incident beam orientation, it has been shown [27] that Fe^{3+} occupy octahedral sites while Fe^{2+} occupy tetrahedral sites in a naturally occurring chromite spinel (Figure 6).



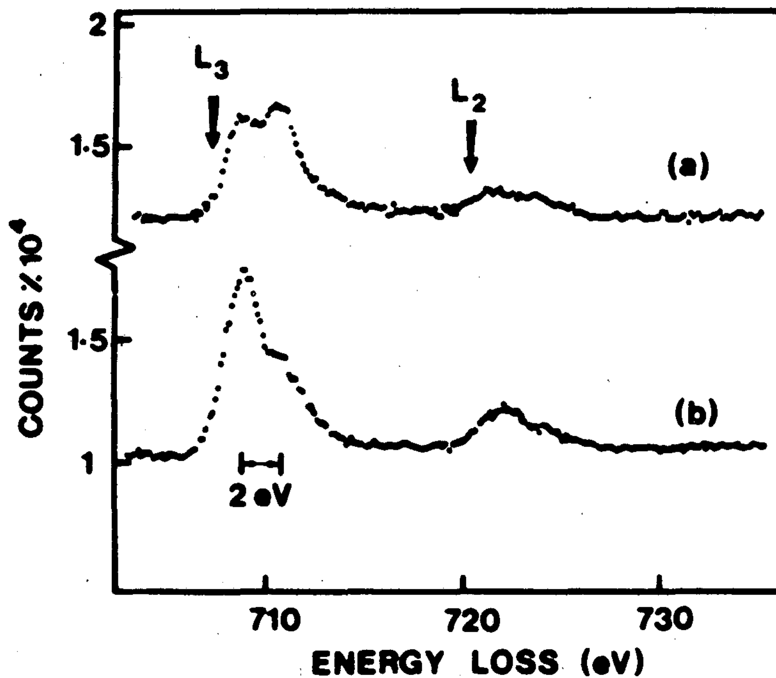


Fig. 6. EEL spectra of a chromite spinel measured under two different incident beam orientations. The detection apertures were shifted parallel to the (400) Kikuchi band such that, by selectively detecting only the high angle scattered electrons without any change in diffraction geometry, a significant enhancement for the low energy edges was observed. For orientation (a) the octahedral sites were selectively enhanced. For orientation (b), tetrahedral site selectivity is observed. Details of the Fe $L_{2,3}$ edge for the same orientations (bottom). The higher energy Fe^{3+} peak is enhanced when the electron beam is localized on the octahedral sites. Such chemical shifts (2eV) can be routinely observed using a LaB_6 filament and a commercial spectrometer [27].

ACKNOWLEDGEMENTS

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