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A GENERALIZATION OF ATOM LOCATION BY CHANNELLING ENHANCED MICROANALYSIS

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ABSTRACT

The technique of atom location by channelling enhanced microanalysis (ALCHEMI), has limitations in practical application. A generalization of this technique, with the underlying idea that additional relationships can be generated by performing these experiments at an appropriate number of orientations depending upon the stoichiometry of the original compound has been developed. The precise number of orientations required to solve the distributions in a whole class of related compounds is expressed in terms of the stoichiometry of the original compound along with the alloying additions.

INTRODUCTION

Ever since the discovery by Borrmann [1] of the orientation dependence of characteristic x-ray emissions, it has been suggested [2] that this dependence could be a potential tool to determine specific site occupations in single crystals. For an incident plane wave of electrons, in

the general case, this requires a knowledge of the dynamical electron wave function and stringent calibration of the electron microscope. Until recently these limitations had impeded the development of a meaningful technique. However, it has been shown [3] that for certain systematic or "planar channelling" conditions, the characteristic x-ray emissions induced by the channelling or blocking of the incident electrons, can provide information on the occupancy of specific crystallographic sites, provided that an a priori knowledge of the distribution of some reference elements is available. This is particularly applicable for crystals with a layered structure (i.e. crystals that in some crystallographic projection can be resolved into alternating layers of parallel non-identical planes [A,B,A,B,...], each plane containing one or more specific crystallographic sites), where the appropriate systematic orientation can be determined by mere inspection. For example the spinel structure compounds can be resolved in the [001] projection into alternating planes of tetrahedral and octahedral sites and hence a $\bar{g} = 400$ systematic orientation is an appropriate one.

However, there are some limitations of this technique. If the crystal structure is not layered, then it is not obvious by mere inspection which systematic orientations are specific site sensitive. In such cases, the electron-induced characteristic x-ray emission intensities, for different site occupations and different incident beam directions, have to be calculated [4]. From these calculations, the appropriate systematic or "planar channelling" condition applicable to that particular crystal structure is determined and the experiment performed [5]. On the other hand, in the original formulation of this technique [3], the site occupancies are

determined by a judicious choice of reference atoms (one for each plane A and B) in the original compound based on some a priori knowledge of their distributions. In many practical alloys/compounds it might not be possible to choose reference atoms that are uniquely distributed on one and only one of the two alternating crystallographic planes. Further, the alloying concentrations might be large enough to alter the distributions of the constituent elements in the original compounds, thereby invalidating the practice of using the original concentrations as internal reference standards.

In this paper a generalization of this technique of ALCHEMI [3] is discussed which overcomes the above limitations as applied to layered structure compounds. The problem is formulated differently by incorporating the stoichiometry of the original compound. Finally, experimental conditions necessary to solve some specific problems are presented.

FORMULATIONS AND ANALYSIS

It is required to determine the crystallographic distributions (site occupancies) in a stoichiometric compound $(Z_i)_{n_i} (X_j)_{m_j}$ where

Z_i - elements of known distributions in the ideal compound
before alloying additions; $(i=1,\dots,r)$

and

X_j - alloying elements, unknown distributions $(j=1,\dots,s)$

For the projection of interest, let the crystal structure be separable into non-identical, alternating, parallel planes (A,B,A,B,...). Now define

- M_{Z_i} - total number of available sites for element Z_i per unit cell in the ideal compound.
- $f_{Z_i, X_j}^{A, B}$ - fraction of available sites for element (Z_i, X_j) on planes (A, B) respectively, per unit cell.
- C_{Z_i} - concentration of element Z_i on plane B to be determined in the non-ideal case, i.e. after alloying additions.
- $(1 - C_{Z_i})$ - concentration of element Z_i on plane A
- M_{X_j} - total number of available sites per unit cell for element X_j in the alloy.
- C_{X_j} - concentration of element X_j on plane B, also to be determined.
- $(1 - C_{X_j})$ - concentration on plane A
- and
- q - number of formula units of $(Z_i)_{n_i} (X_j)_{m_j}$ per unit cell.

From the crystal structure, for complete occupation of all the crystallographic sites on plane B, an occupancy balance can be written

$$\sum_{i=1}^r n_i C_{Z_i} + \sum_{j=1}^s m_j C_{X_j} = \frac{1}{q} \sum_{i=1}^r M_{Z_i} f_{Z_i}^B \quad (1)$$

The characteristic x-ray emission intensity (N) for any element Z_i in the orientation (η) is expressed as a linear sum of the contributions from each of the parallel planes (A,B,A,B,...)

$$N_{Z_i}^{(\eta)} = P_{Z_i} f_{Z_i}^A M_{Z_i} (1 - C_{Z_i}) I_A^{(\eta)} + P_{Z_i} f_{Z_i}^B M_{Z_i} C_{Z_i} I_B^{(\eta)} \quad (2)$$

where $I_{A,B}^{(\eta)}$ is the effective Bloch wave intensity in planes (A,B) for the orientation (η) and P_{Z_i} is the scaling factor for element Z_i .

Similarly for alloying element X_j ,

$$N_{X_j}^{(\eta)} = P_{X_j} f_{X_j}^A M_{X_j} (1 - C_{X_j}) I_A^{(\eta)} + P_{X_j} f_{X_j}^B M_{X_j} C_{X_j} I_B^{(\eta)} \quad (3)$$

Now define a normalized measure of the orientation dependence

$$\mathcal{R}(\eta_1, \eta_k, Z_1 X_j) = \frac{\frac{N_{Z_1}^{(\eta_1)}}{N_{X_j}^{(\eta_1)}}}{\frac{N_{Z_1}^{(\eta_k)}}{N_{X_j}^{(\eta_k)}}} \quad (4)$$

where

η_1 is any one fixed orientation;

η_k are the orientations η_2 through η_T (excluding η_1)

η_T is the total number of orientations to be determined by this analysis,

and

Z_1 is any one arbitrarily fixed original constituent.

The numerator of this normalized measure $\mathcal{R}$ is a ratio of the counts for one of the original elements to that of an alloying element at an arbitrary given fixed incident beam orientation. The denominator is the same ratio, but at any one of the other orientations $\eta_2 \dots \eta_T$.

Substituting from (2) and (3) one obtains

$$\mathcal{R}(\eta_1, \eta_k, Z_1, X_j) = \left\{ \frac{f_{Z_1}^A (1 - C_{Z_1}) + f_{Z_1}^B C_{Z_1} \beta_1}{f_{X_j}^A (1 - C_{X_j}) + f_{X_j}^B C_{X_j} \beta_1} \right\} \times \left\{ \frac{f_{X_j}^A (1 - C_{X_j}) + f_{X_j}^B C_{X_j} \beta_{j,k}}{f_{Z_1}^A (1 - C_{Z_1}) + f_{Z_1}^B C_{Z_1} \beta_{1,k}} \right\} \quad (5)$$

where

$$\beta_k = \frac{I_B^{(\eta_k)}}{I_A^{(\eta_k)}} \quad (6)$$

The factor $\mathcal{R}(\eta_1, \eta_k, Z_1, X_j)$ is experimentally determined. One can define, for fixed η_1 and Z_1 , $s(\eta_1 - 1)$ such independent factors or equations.

However, for each orientation η_k , the relationship

$$\frac{N_{Z_i}^{(\eta_k)} (i \neq 1)}{N_{Z_1}^{(\eta_k)}} = k_{1,i} \frac{I_A^{(\eta_k)} f_{Z_i}^A (1 - C_{Z_i}) + I_B^{(\eta_k)} C_{Z_i} f_{Z_i}^B}{I_A^{(\eta_k)} f_{Z_1}^A (1 - C_{Z_1}) + I_B^{(\eta_k)} C_{Z_1} f_{Z_1}^B} \quad (7)$$

is obtained. This equation (7) represents the ratio of the counts of one of the original elements (Z_i) at a given orientation (η_k) to the counts of an arbitrarily selected original element (Z_1) at the same orientation. Here

$$k_{1,i} = P_{Z_i} M_{Z_i} / P_{Z_1} M_{Z_1}$$

and is the corresponding ratio of the scaling factors multiplied by the total number of available sites per unit cell for the same two elements. This on rearrangement, gives

$$\beta_k = \frac{f_{Z_i}^A (1 - C_{Z_i}) - f_{Z_1}^A (1 - C_{Z_1}) \left[\frac{N_{Z_i}^{(\eta_k)}}{N_{Z_1}^{(\eta_k)}} \right] \frac{1}{k_{1,i}}}{\left[\frac{N_{Z_i}^{(\eta_k)}}{N_{Z_1}^{(\eta_k)}} \right] \frac{1}{k_{1,i}} f_{Z_1}^B C_{Z_1} - f_{Z_i}^B C_{Z_i}} \quad (9)$$

Again, for every pair (Z_1, Z_i) ($i \neq 1$) one can define η_T equations of the type (7), giving rise to a total of $(r-1)\eta_T$ such independent factors or equations.

To determine β_k , it is essential to do an experiment under a non-channeling condition, preferably when the condition $I_A \simeq I_B$ is satisfied. As a strong dynamical scattering is a prerequisite for any orientation dependence, this condition can be achieved under a kinematical diffraction condition, which is characterized by the absence of the strong excitation of any of the lower order diffraction vectors. [It is recognized that even though ideally one would prefer that $I_A = I_B$, only the approximate identity can be established in experimental practice because the structure factors for the two planes f_A and f_B are not equal, i.e. $f_A \neq f_B$]. Then for such an orientation (nc):

$$\frac{N_{Z_i}^{(nc)}}{N_{Z_1}^{(nc)}} = \frac{P_{Z_i} M_{Z_i} f_{Z_i}^A (1 - C_{Z_i}) + P_{Z_i} M_{Z_i} f_{Z_i}^B C_{Z_i}}{P_{Z_1} M_{Z_1} f_{Z_1}^A (1 - C_{Z_1}) + P_{Z_1} M_{Z_1} f_{Z_1}^B C_{Z_1}} \quad (10)$$

which implies that

$$k_{1,i} = \left[\frac{N_{Z_i}^{(nc)}}{N_{Z_1}^{(nc)}} \right] \left[\frac{f_{Z_1}^A (1 - C_{Z_1}) + f_{Z_1}^B C_{Z_1}}{f_{Z_i}^A (1 - C_{Z_i}) + f_{Z_i}^B C_{Z_i}} \right] \quad (11)$$

which can be substituted in equation (9).

Therefore, in the general case, there are 's' unknowns in the concentrations C_{X_j} , 'r' unknowns in the concentrations C_{Z_i} and η_T unknowns in the ratios of Bloch wave intensities $I_B^{\eta_k}/I_A^{\eta_k}$. The number of equations of the types (5) and (7) along with the occupancy balance equation (1) required to unequivocally solve for the above number of unknowns can be generated if and only if η_T satisfies:

$$\eta_T = \frac{2s + r - 1}{s + r - 2}$$

RESULTS AND DISCUSSIONS

For an original compound of 'r' elements Z_i with 's' alloying elements X_j , the number of orientations η_T at which the characteristic x-ray emission intensities have to be measured in order to unequivocally determine the distribution of the constituent elements after alloying in the different crystallographic sites is given in Table 1.

TABLE 1

NUMBER OF ORIGINAL ELEMENTS (r)	NUMBER OF ALLOYING ELEMENTS (s)	REQUIRED NUMBER OF ORIENTATIONS (n_T)
1	2	4
1	3	3
2	1	3
2	2	non-integer
3	1	2
3	2	2
3	3	2
3	4	2

From Table 1 it can be seen that in this generalization, specific site occupations can be determined for almost all practical cases. The $r=2, s=2$ case is an exception for which this analysis gives a non-physically realizable result. [However, even this exceptional case can be solved [6] if one of the reference elements is confined to only one of the two alternating planes.] As opposed to the original formulation, where an a priori knowledge of the distributions of two reference elements is required for the analysis (it is also assumed that these distributions also remain unchanged on alloying) in this generalization, all that is required is an exact idea of which site a particular element can occupy, whether it is a reference or alloying addition and not the actual distribution. Finally, it can also be shown [4] that the original ALCHEMI formulation can be derived from this generalization when the corresponding assumptions mentioned earlier are taken into account.

The applicability of this technique is subject to the condition that the material has a layered structure, e.g. compounds with a spinel structure, $\text{Sm}_2(\text{CoTM})_{17}$ compounds, etc. Further, the "systematic" excitation or "planar channelling" condition is always maintained and all tilting is done along this systematic direction. Orientations close to the normal to the systematic line and at angles corresponding to a small positive or negative excitation error of low order Bragg reflections are sufficient. Finally, it must be pointed out that even in this formulation, only distributions on specific planes rather than on specific sites can be determined, unless a specific plane exclusively harbours a specific site in that particular crystallographic projection. In the general case, however, site occupations can be unequivocally determined by performing these experiments using a linearly independent set of diffraction vectors.

The advantages and limitations of using the orientation dependence of characteristic x-ray emission in site occupation studies have been discussed elsewhere [3]. The limitations of conventional energy dispersive x-ray microanalysis confine this technique to elements heavier than Na, unless windowless or thin film window detectors are employed. This entire analysis presented here rests on the assumption that the scattering processes leading to x-ray production are highly localized. For inner shell excitations sufficient evidence exists [7,8] to validate this assumption. As the technique is formulated in terms of characteristic x-ray intensity ratios, no parameters nor any knowledge of the dynamical wavefunction are required. This, combined with the relative ease with which an energy dispersive x-ray spectra can be collected and analyzed, makes this generalized technique superior to other conventional ones. Finally, the whole analysis is independent of both thickness and local orientation.

CONCLUSIONS

In this paper a generalized technique of atom location by channelling enhanced microanalysis has been presented that is applicable to layered crystal structures. The limitations of a similar technique formulated earlier have been overcome and experimental conditions required to solve a whole range of related problems have been presented.

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