Title

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ABSTRACT

The dependence of electron induced characteristic x-ray emissions on both the orientation and the acceleration voltage for $MgAl_2O_4$ have been calculated. A non uniform voltage dependence, characterized by an 'inversion' voltage is predicted. The characteristics of this 'inversion' voltage is shown to be different from the conventional critical voltage effect.

INTRODUCTION

As a result of dynamical scattering of an incident plane wave of electrons, a standing wave pattern is set up within the crystal unit cell. For a given crystal, depending on the orientation, this intensity modulation will be a maximum on certain crystallographic sites. Hence, the intensities of highly localized scattering events such as inner shell excitations, show a strong orientation dependence [1,2]. Under favourable conditions, this orientation dependence of characteristic x-ray emissions can be exploited to obtain crystallographic information, particularly with respect to the determination of the specific site occupancy of the constituent elements [4,5,6]. In this paper, the influence of the acceleration voltage is discussed as an independent parameter on this orientation dependence, based on calculations.

THEORETICAL FORMULATION

This theory assumes that the characteristic x-ray emission of element x at the coordinate $\bar{\rho}$ in the unit cell is proportional to (a) the intensity of the electron standing wave at $\bar{\rho}$ and (b) the probability of the localization of the scattering event at $\bar{\rho}$, i.e, $P(\bar{\rho})$. For the approximation that $P(\bar{\rho})$ is highly localized, i.e., a delta function at the mean atomic positions, for a crystal of thickness 't':

$$N_x = \sum_{RSI} \int_o^t \Phi^* \Phi \, dz \qquad (1)$$

where N_x is the intensity of the characteristic x-ray emission of element x and the summation is over the relevant crystallographic sites of interest. Here Φ is the scattered wave amplitude at any depth z expressed as a linear combination of Bloch waves, for the case of an incident plane wave, in the conventional dynamical theory formulation [7].

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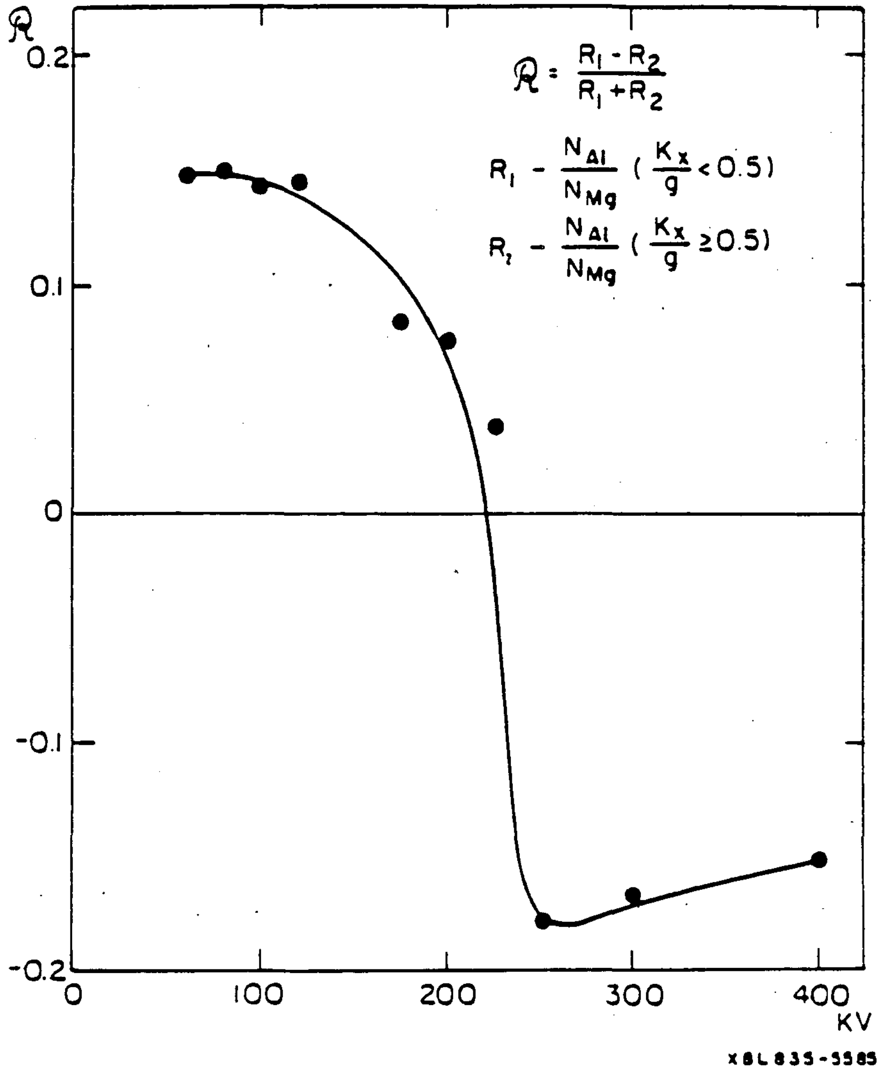

Fig. 1. Variation of the electron induced charateristic x-ray emissions with both orientation and acceleration voltage. Calculations were performed for 15 beams, systematic excitation condition (g = 400).

On carrying out the integration and rearranging the various terms, one can express the characteristic x-ray intensity/unit thickness as:

$$N_z = \sum_{RSI} [\sum_{g,h} \exp (\bar{h} - \bar{g}) \cdot \bar{x}) \{ \sum_{\substack{j,1 \\ j=1}} C_o^{(j)*} C_g^{(j)*} C_o^{(1)} C_h^{(1)}$$

$$+ \sum_{\substack{j,1 \\ j>1}} C_o^{(j)*} C_g^{(j)*} C_o^{(1)} C_h^{(1)} \frac{\mathrm{Sin}[(k_z^{(j)} - k_z^{(1)} t]}{(k_z^{(j)} - k_z^{(1)})t} \}] \quad (2)$$

where $C_h^{(j)}$ are the Bloch wave coefficients and $k_z^{(j)}$ are components of the wave vector for the electrons in the crystal. (A more detailed exposition of the theoretical formulation is given elsewhere [8].)

RESULTS AND DISCUSSIONS

Using the above expression (2), electron induced characteristic x-ray emission intensities were computed for $MgAl_2O_4$. This compound has a spinel structure, which in the (100) projection can be separated into alternate planes of Aluminium atoms (octahedral coordination) and magnesium atoms (tetrahedral coordination). Calculations were done for a 15 beam (g=400) systematic excitation condition, over a range of orientations ($0 \leq K_x/g \leq 1.0$) and acceleration voltages (60-400kV). Figure 1 discribes the variation of the intensities of the characteristic x-ray emissions as a function of both orientation and acceleration voltage. The ordinate R is a normalized measure of the orientation dependence and is defined as $R = (R_1 - R_2)/(R_1 + R_2)$ where R_i is the ratio N_{Al}/N_{Mg} at their corresponding positions of extrema and i takes the value 1 or 2 for orientations with $k_x/g < 0.5$ and $k_x/g \geq 0.5$ respectively. A positive value of R signifies a maxima of the characteristic x-ray intensity of Mg (N_{Mg}) for some orientation with $k_x/g \geq 0.5$ and a minima for $k_x g < 0.5$. It also signifies an exactly opposite behavior for N_{Al}. The prediction of the orientation dependence at 100 kV is in agreement with experimental results [6]. However, it can be seen, that at higher acceleration voltages, this orientation dependence though not particularly enhanced in magnitude, exhibits an interesting reversal in character, i.e., above some 'inversion' voltage the orientation dependence of N_{Al} and N_{Mg} are interchanged, and in Fig. 1, this is represented by R taking negative values. Moreover, the orientation of a minimum or maximum also varies slightly with the acceleration voltage.

In order to isolate the role of the acceleration voltage alone, the variation of the ratios of the characteristic x-ray intensities as a function of the acceleration voltage were calculated for a number of different orientations. These were normalized in the same manner as done earlier (with $R_1 = N_{Al}/N_{Mg}$ at the orientation of interest, k_x/g and $R_2 = N_{Al}/N_{Mg}$ at a non-channelling symmetric orientation) and plotted (Fig. 2). From this plot, one can infer that at the 'inversion' voltage, these normalized ratios of intensities do indeed undergo a reversal in character (sign) at all orientations, though the effect is more pronounced as k_x/g increases. This suggests that one can use this voltage dependence to determine qualitatively, site occupations of elements in crystals provided that this 'inversion' voltage is known in advance.

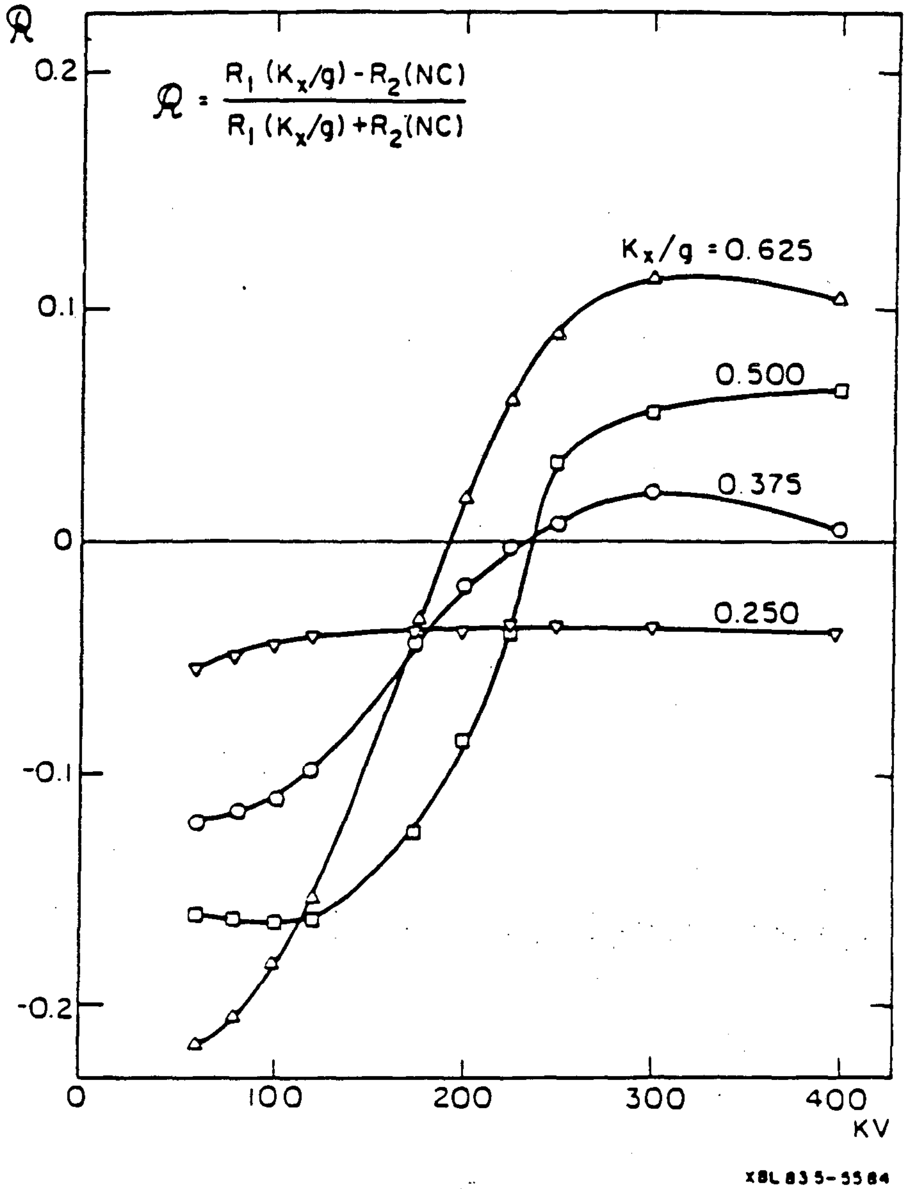

Fig. 2. Variation of the electron induced characteristic x-ray emissions as a function of the accelaration voltage for fixed excitation errors. Normalization is done with respect to a non channelling (NC) symmetric orientation.

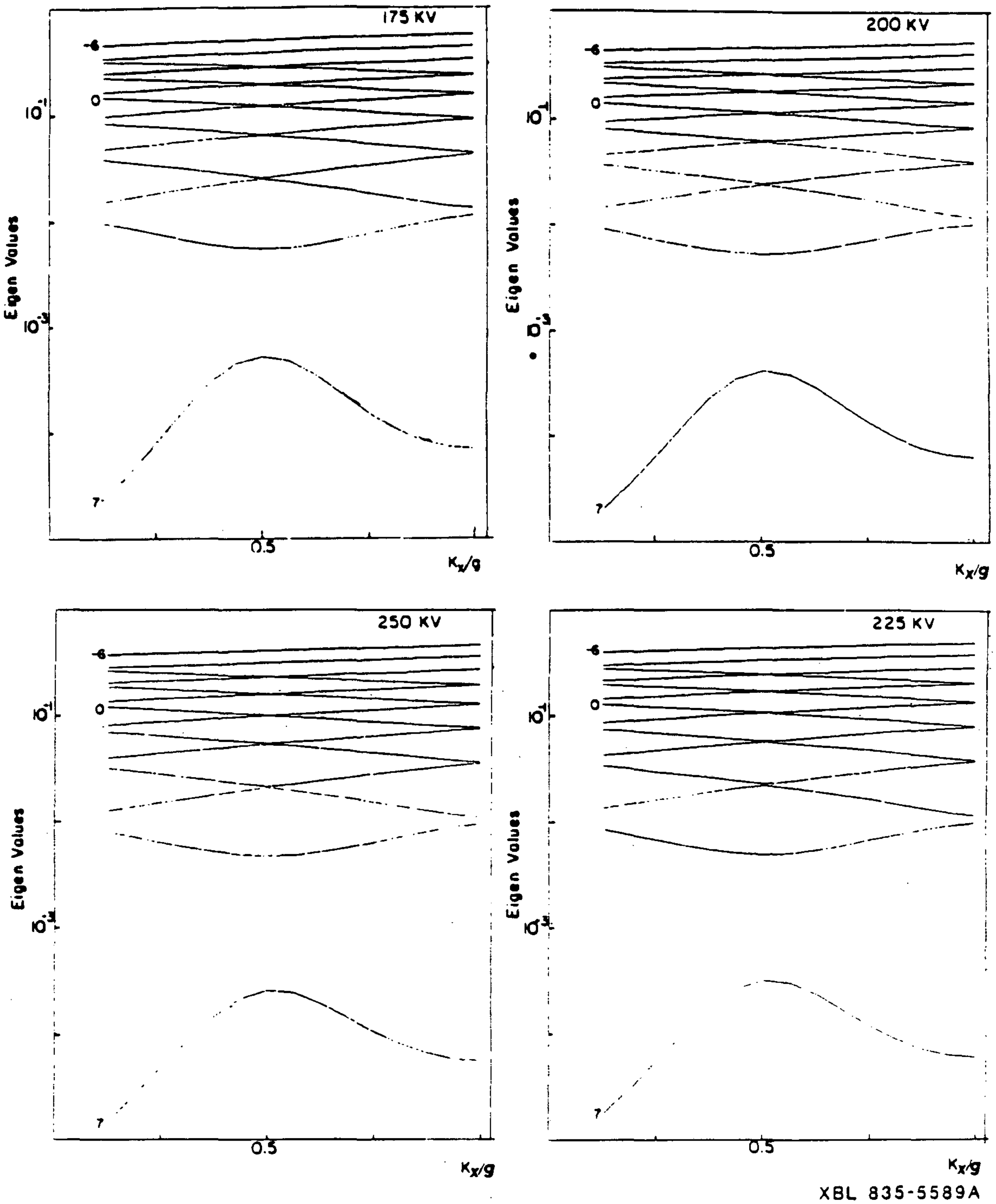

Fig. 3. Dispersion surfaces [Eigen values of the Bloch waves vs. orientation (k_x/g)] for different acceleration voltages.

According to Lally, et al. [9], for a centrosymmetric crystal set at the symmetric Laue position for the reflection $2\bar{g}$, a change in the symmetries and excitation amplitudes of the Bloch waves is observed, at a particular critical voltage characteristic of the crystal. An alternative way of interpreting this is that at the critical voltage, the eigenvalues of the Bloch waves become degenerate. In Fig. 3, the dispersion surfaces have been plotted, calculated at 25 kV intervals over the voltage range of interest with the thickness, t modified at each voltage such that λt is a constant. These dispersion surfaces indicate that for this particular case of the crystal oriented at the reflection $1\bar{g}$, exact or with positive or negative excitation errors, no observable degeneracy in the eigenvalues of the Bloch waves are present. This indicates that the nature of this sensitivity of the electron induced characteristic x-ray emissions to the acceleration voltage which we term as the 'inversion' voltage is different from the conventional critical voltage effect. However, a change in orientation or voltage should have similar effects in so far as they independently change the diagonal elements of the dynamical scattering matrix. Further calculations and experiments are in progress to understand this anamoly.

CONCLUSION

It has been shown that the electron induced characteristic x-ray emmissions, apart from being orientation dependent are also voltage dependent. This voltage dependence is not uniform but exhibits an 'inversion' behavior, which for $MgAl_2O_4$ is predicted to be between 175-250 kV. It appears that this sensitivity to voltage can be used to determine qualitatively site occupations of elements in crystals as an alternative to the orientation dependence. The exact nature of this 'inversion' voltage seems to be anamolous for it exhibits characteristics different from the conventional 'critical' voltage effect.

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