IONIZATION DELOCALIZATION AND ALCHEMI OF B2-ORDERED ALLOYS

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Recent formulations of the ALCHEMI technique have explicitly accounted for ionization delocalization of an element i with a single linear parameter L_i that represents the extent of localization.^{1,2} The x-ray emission of a spectral line characteristic of the element is assumed to be proportional to a linear combination of the thickness-averaged electron intensity at (1) the site of the atom (fraction: L_i) and (2) averaged over the unit cell (fraction: $(1 - L_i)$). The parameter L_i is assumed to be characteristic of the elemental shell and independent of the diffracting conditions. In consequence of these assumptions, it has been shown that ionization delocalization correction can be performed in conjunction with "statistical" ALCHEMI by correcting only the extracted correlation coefficients.²

The parameter $r_i(\xi) = I_i(\xi) / I_i(0)$ is defined to be the ratio of the characteristic intensity (I) of element i at a crystal orientation (ξ) to its characteristic intensity at a reference orientation (0), which is ideally free of electron channeling effects. Coefficients α_{kj} correlating the r -values of each alloying element k with those of the n host elements j are extracted using multivariate analysis following Rossouw et al.,³

$$r_k = \sum_{j=0}^n \alpha_{kj} r_j, \quad (1)$$

except with an additional coefficient α_{k0} to account for the delocalized fractions of each element, with $r_0 \equiv 1$.¹ The correlation coefficients can be corrected for ionization delocalization with the relation:²

$$\chi_{kj} = \frac{L_j}{L_k} \alpha_{kj} \equiv L_{jk} \alpha_{kj}. \quad (2)$$

These corrected coefficients equal the fractional occupancies p_{kj} of alloying element k on site j if the host elements are perfect markers for their respective sites. Whether the host elements are perfect markers or not, the sum of χ_{kj} over all sites j should equal unity, just as the site occupancies sum to unity. The purpose of the present paper is to demonstrate that the major assumption underlying this formulation is justified: that the degree of ionization localization of an elemental shell can be accounted for by a linear coefficient; and to introduce a potential method, which would be applicable to B2-ordered alloys, of independently extracting the ratio of coefficients L_{jk} necessary for delocalization correction.

For B2-ordered alloys, the major low-index planes are $\{110\}$ and $\{200\}$. The $\{110\}$ planes are of equal composition: for a stoichiometric alloy AB, the composition of each $\{110\}$ plane is AB (Fig. 1). Conversely, the two crystallographic sites are completely separated on alternating $\{100\}$ planes and have alternating compositions A and B in a fully ordered alloy. When dynamical diffracting conditions are set up at these two systematics orientations, $\{200\}$ should provide good discrimination between the 'A' and 'B' sites of the crystal and $\{110\}$ none at all, as long as contributions from nonsystematic reflections are insignificant. Ionization delocalization should influence the variation of the characteristic x-ray intensities at both planar channeling conditions. However, at the $\{110\}$ systematics orientation, the effect of ionization delocalization should be isolated.

A Cr-doped FeAl alloy of nominal composition $\text{Fe}_{60}\text{Al}_{35}\text{Cr}_5$ and a series of Fe-doped NiAl alloys with between 0.25 and 12 at.% Fe were analyzed for this study. Energy-dispersive x-ray (EDX) spectra were acquired with a Philips CM12 operated at 120 kV equipped with an EDAX 9900 spectrometer and superUTW Si(Li) detector. The variation of r -values of the host elements Fe and Al relative to that of the alloying element Cr is shown in Fig. 2 for spectra acquired near $\langle 117 \rangle$ beam direction at a range of $\{110\}$ excitations between the symmetry and the $\{220\}$ Bragg orientations. The slopes of these lines, which are the ratios L_{jk} for the $\{110\}$ systematics orientation, are shown in Fig. 2. These values, which indicate that Fe is slightly more localized and Al substantially less localized than Cr, are plausible. The excellent linearity of the data substantiates the use of linear coefficients to model ionization localization.

Furthermore, it has been investigated whether the L_{jk} acquired at a $\{110\}$ systematics orientation could be accurately applied to ALCHEMI data acquired at $\{200\}$. Other studies have indicated that the degree of localization varies with interplanar spacing, and that this variation may be strong for lower energy ionizations such as Al K.⁴ Correlation coefficients α_{kj} acquired at $\{200\}$ were corrected with L_{jk} ratios determined at $\{110\}$, as indicated by equation (2). This method yields independent χ_{kj} , and one can check to ensure that their sum, $\Sigma \equiv \chi_{CrFe} + \chi_{CrAl}$ is unity. It would be expected that a significant difference in L_{Al} between $\{110\}$ and $\{200\}$ would effect a significant deviation of Σ from unity, particularly for alloys in which the alloying element resides predominantly on the 'Al'-site. This test was performed by applying the L_{jk} ratios in Fig. 2 to ALCHEMI data acquired from the Cr-doped FeAl specimen near $\langle 014 \rangle$ beam direction at a range of $\{200\}$ excitations between symmetry and the $\{400\}$ Bragg position. The result is $\Sigma = 1.04 \pm 0.03$. Similarly, localization coefficients L_{jk} were extracted from an alloy of stoichiometry $Ni_{50}Al_{40}Fe_{10}$ and applied to the correlation coefficients of a series of sixteen Fe-doped NiAl alloys. The result of this more extensive study is $\langle \Sigma \rangle = 1.01 \pm 0.01$. Also, there was no measurable variation in the Σ values with site-occupancy. These results seem to be in better agreement with similar L_{jk} for the $\{110\}$ and $\{200\}$ systematics orientations than with L_{jk} that vary significantly with interplanar spacing. The outlined method for delocalization correction would allow accurate ALCHEMI analyses that are free from reliance on adjustable parameters.⁵

References

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FIG. 1. Schematic representation of a B2-ordered alloy "AB" viewed along $\langle 001 \rangle$.
 FIG. 2. Variation of the intensity ratios of the host and alloying elements in Cr-doped FeAl for $\{110\}$ systematics orientation. The values L_{jk} are the slopes of the linear regression fits to the data.

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