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THE ROLE OF ALCHEMI IN UNDERSTANDING THE PROPERTIES OF ORDERED INTERMETALLIC ALLOYS

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ABSTRACT

After one and one-half decades of development, ALCHEMI is approaching the status of an established analytical technique. Many of the problems that have plagued ALCHEMI, especially for the analysis of ordered intermetallic alloys, are now well understood, and accurate site-distributions can be extracted from a variety of intermetallic alloys. This paper begins with an overview of the factors that can lead to large systematic errors or gross misinterpretations of ALCHEMI data, with illustrations from a variety of ordered intermetallic alloys. The paper concludes with a discussion of ALCHEMI in the broader context of understanding the properties of ordered intermetallic alloys. The results of systematic studies are used to illustrate the role of ALCHEMI in determining the competing effects of thermodynamic and kinetic factors during alloy processing and the correlation of alloy properties with the atomic site distributions on which the properties ultimately depend.

INTRODUCTION

Since the introduction of the ALCHEMI technique as a method for determining the atomic site distributions [1,2], our understanding of the factors that affect the reliability of ALCHEMI has greatly improved. Early innovations were introduced to improve the statistical basis of ALCHEMI measurements [3,4]. However, the reliability of ALCHEMI for analyzing ordered aluminide intermetallics remained poor because of the phenomenon of ionization delocalization [5,6], which sometimes resulted in nonphysical site occupancies [5,7]. The first explicit correction for ionization delocalization was introduced after about a decade of ALCHEMI studies [8], followed by corrections for antisite defects [9]. ALCHEMI has now been formulated to account for all of these factors [10]. The reliability of this improved formulation has been tested by applying it to a wide variety of ordered intermetallic alloys and by conducting systematic studies on series of related alloys, to test the consistency of the results obtained. Some of these applications are used in this paper to illustrate the reliability of the improved ALCHEMI formulation. The site distributions for alloying additions as dilute as 0.25 at.% have been successfully measured, and precisions better than ±1% (on a site-occupancy scale from 0 to 100%) have been routinely achieved for alloying additions at the 10 at.% level. The status of ALCHEMI is now approaching that of an established analytical technique, where accurate site-occupancies are routinely acquired from a variety of ordered intermetallic alloys.

The basis of ALCHEMI (atom location by channeling enhanced microanalysis) is contained within its acronym. ALCHEMI is a diffraction-based technique that relies on electron channeling (or dynamical electron diffraction or elastic scattering). The ALCHEMI effect arises because the electron channeling differs on the various sublattices of an ordered alloy as a function of channeling orientation. However, the effect is measured by recording the variations of characteristic X-ray intensities of the elements composing the alloy. ALCHEMI is thus a spectroscopic technique, which distinguishes the signals that arise from the different elements. (By comparison, conventional X-ray diffraction analysis does not distinguish between the different elements, but only measures the average signal from the different sublattices.) The first section of this paper examines factors that affect the reliability of ALCHEMI measurements.

FACTORS AFFECTING THE RELIABILITY OF ALCHEMI

There are many factors that affect the accuracy of the site distributions measured with ALCHEMI, and hence the reliability of the results of the technique. This first section of the paper discusses factors that can lead to large systematic errors or gross misinterpretations of ALCHEMI data. This list is not exhaustive. Issues that should concern the analyst, such as the importance of monitoring the beam current during analysis, of choosing channeling conditions that do not excite nonsystematic reflections, and of a proper statistical treatment of the data have been outlined elsewhere [11] and are not treated here. Rather, this section covers issues that can be used by the nonspecialist to evaluate the reliability of reported site distributions in the literature.

Microanalysis standard for quantification

The extraction of accurate quantitative chemical information from a specimen using a microanalysis technique usually requires a standard of some kind. For example, for the case of electron probe microanalysis, arguably the most established microanalysis technique, quantitative compositions to within a few percent relative can be extracted from an unknown compound by using pure element standards similar in average atomic number to the unknown [12]. The comparable standard for X-ray microanalysis of electron-transparent specimens in the analytical electron microscope (AEM) are microanalysis k-factors, which are usually determined from thin specimens of known composition [13]. For both techniques, it is widely accepted that the accuracy of the technique increases as the standard becomes closer in composition to the unknown, as long as the standard itself is reliable.

For ALCHEMI, we have the ultimate microanalysis standard: a spectrum acquired from the specimen when channeling is negligible, during the same experiment that the channeling data are acquired, without reorienting the specimen and under identical acquisition conditions (such as beam current). Using this "self normalization" scheme, the channeling response for a given element is quantified by normalizing the characteristic intensity $I_i^{(\xi)}$ of an element i acquired at a given channeling condition (ξ) to the corresponding intensity $I_i^{(0)}$ acquired when channeling is negligible (0):

$$r_i^{(\xi)} - 1 = [I_i^{(\xi)} - I_i^{(0)}] / I_i^{(0)} .$$

Note that the quantity ($r_i^{(\xi)}$ - 1) is zero by definition for (ξ) = (0), and positive (negative) when the channeling-modified intensity is greater (smaller) than that in the absence of channeling.

The use of the specimen itself as the microanalysis standard makes it unnecessary to measure k-factors and circumvents many of the factors that degrade the accuracy of (compositional) X-ray microanalysis in the AEM [13]. These include factors intrinsic to the standard such as its compositional integrity, as well as extrinsic factors that differ between specimen and standard such as surface films, which are especially common for electropolished specimens. These factors are obviously identical for specimen and standard when the self normalization scheme is used. Other factors severely degrade the accuracy of quantifying elements with soft X-ray lines, such as Al-K. These factors include changes in detector efficiency over time (due, for example, to the buildup of contaminants such as ice on the detector) and the calculation of absorption effects for soft X-rays. The detector efficiency is the same because the standard and specimen are measured during the same experiment; the absorption behavior is identical because (i) the composition of specimen and standard are identical and (ii) the orientation of the specimen relative to the X-ray detector, which affects the X-ray absorption path length, is unchanged between the measurement of specimen and standard. It should be noted that not all recent formulations of ALCHEMI use this self-normalization scheme, despite its obvious advantages, but rather incorporate microanalysis k-factors obtained from standards [14,15].

Electron channeling and discrimination between sublattices

ALCHEMI can determine the sublattice occupancy of alloying elements in an ordered alloy when the channeled electron intensities on the two sublattices vary independently. This independent variation occurs only when one or more superlattice reflections of the alloy is strongly excited. For example, in B2-ordered alloys at the (200) systematic orientation, the (100) superlattice reflection must be strongly excited in order for there to be good discrimination between the 'A' and 'B' sites [11]. At orientations where the (100) reflection is weakly excited (i.e., with a large positive excitation error on (100), producing a "weak beam" condition), such discrimination is absent, and any variation in the characteristic X-ray intensities occurs because of ionization delocalization (discussed in the next section) rather than because of site discrimination.

There are two situations for which the superlattice reflection can never be strongly excited. The first is trivial: if the alloy is fully disordered, so that all lattice sites are equivalent, then the superlattice reflection disappears – B2-order reverts to disordered bcc, and the (100) reflection is forbidden. For this case, there is no channeling discrimination between the sites because the sites are identical. However, the superlattice reflection can also disappear even if the alloy is fully ordered, if the elastic scattering powers of the two sublattices are similar. For example, for B2-ordered alloys AB, the structure factors of all superlattice reflections are of the form $f_{super} = (f_A - f_B)$. As a rule of thumb, elastic scattering powers scale qualitatively with atomic number Z [16]. When there is a large difference between the elastic scattering factors of the host elements, as is the case for NiAl, substantial discrimination would be expected between the sublattices for almost all analyses. However, for the case of FeCo, the discrimination between the sublattices would be expected to be weak because the two adjacent transition elements have nearly identical elastic scattering powers. ALCHEMI would not be able to discriminate between the sublattices even for the fully ordered compound. This is not a trivial point, since ALCHEMI studies in the literature have reported site occupancies for alloys such as $L1_2$-ordered Cr-doped Ni_3Fe [9,15], although clearly from the above discussion these alloy site distributions cannot be reliably determined with ALCHEMI.

As an example, consider the C15-ordered Laves phase $Nb_{33}Cr_{42}V_{25}$ at the (800) orientation [17,18]. For most C15-ordered alloys AB_2, the (800) orientation is preferred because the two sublattices of the crystal are completely separated on the alternating planes (A & B_2). The structure factor of the (400) superlattice reflection is $f_{400} = (f_A - 2*f_B)$. However, because the elastic scattering power of the Nb host element is approximately twice that of Cr and V, the (400) superlattice reflection is vanishingly weak, as shown in Figure 1. Accordingly, when ALCHEMI was performed on this alloy at (800), the data were meaningless, and this was reflected by poor precision of the extracted site-occupancy. ALCHEMI analysis was therefore performed at (440), where the alternating planes (AB & B) do not fully separate the two sublattices but for which the structure factor of the (220) superlattice reflection ($f_{220} = f_A$) is substantial. This analysis showed that the fraction of V on the 'Cr' sublattice is $p_{V\text{'}Cr\text{'}} = 99.3\pm3.9\%$. The (400) superlattice reflection has therefore disappeared even though the alloy is fully ordered. Note that for many alloys there is no alternative series of planes that exhibit different channeling behavior, as is the case for the

(800) and (440) series of planes for C15-ordered alloys. Accordingly, there is no way to determine whether the alloy is disordered or whether the alloy is highly ordered with similar elastic scattering factors for the two sublattices. For example, for B2-ordered alloys, all superlattice reflections have the same structure factor, $f_{super} = (f_A - f_B)$. If the (100) superlattice reflection is weak, all other superlattice reflections will also be weak and ALCHEMI cannot be used to extract site distributions.

Alloys having a high concentration of an alloying element with a substantially different elastic scattering factor from the host elements can have a significant effect on the channeling site discrimination. Accordingly, good channeling contrast may be obtained where poor contrast is expected, and vice versa, depending upon the site occupancy of the alloying element. For example, if 20 at.% Pd were added to the FeCo alloy, a strong (100) superlattice reflection, and hence good site-discrimination, would be obtained if Pd partitioned strongly to one of the sublattices. (Note that if the Pd partitions equally, its contributions to the elastic scattering power of the two sublattices balance and no improvement in site-discrimination would be observed.) Conversely, if a similar amount of Pd were substituted for Al in NiAl, the site-discrimination might become more or less pronounced, depending upon the site occupancy of Pd. If Pd were to strongly favor the 'Ni' sublattice, displacing the Ni host element to the 'Al' sublattice with a net site distribution $[Pd_{20}Ni_{30}][Al_{30}Ni_{20}]$, the (100) superlattice reflection, and hence the site-discrimination, would remain strong. However, if Pd were to strongly favor the 'Al' sublattice, producing a net site distribution $[Ni_{50}][Al_{30}\,Pd_{20}]$, the (100) superlattice reflection would become much weaker since the average elastic scattering power of the Al and Pd atoms would be similar to that of Ni. Given this substitution behavior, an ALCHEMI study of alloys in the series $Ni_{50}Al_{50-x}Pd_x$ would be expected to yield good site discrimination both for $x \approx 0$ ($f_{Ni} \gg f_{Al}$) and for $x \approx 50$ ($f_{Ni} \ll f_{Pd}$), but there would be some value of x for which the elastic scattering powers of the two sublattices would compensate one another, so that the superlattice reflection would vanish and the site discrimination would disappear entirely. A likely illustration of this phenomenon is provided by B2-ordered alloys of composition Nb-15Al-xTi [19]. Data published for three alloys

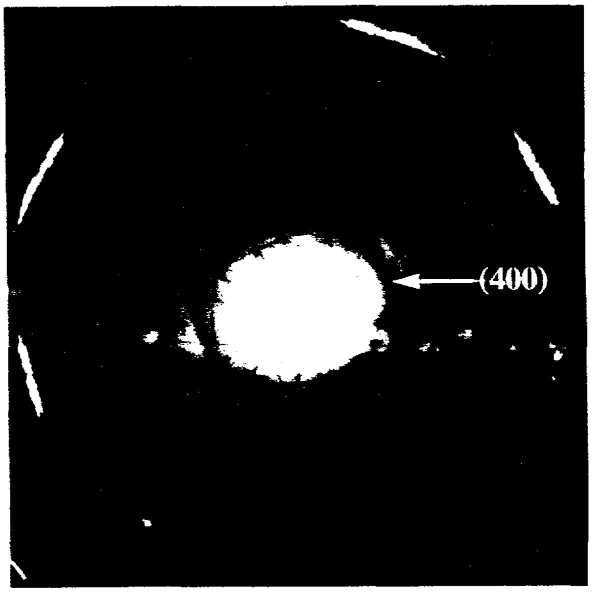


Fig. 1. Convergent beam electron diffraction (CBED) pattern acquired from C15-ordered (AB_2) $Nb_{33}Cr_{42}V_{25}$ at the center of (800) systematic row. The arrow marks the position of the (400) reflection. Because the elastic scattering from the alternating planes (A & B_2) is almost identical, the (400) superlattice reflection is vanishingly weak. Accordingly, ALCHEMI cannot be used at this orientation to determine atomic site-distributions.

with x = {10, 25, 40} show that the channeling effect is significantly smaller for the alloy of intermediate composition, x = 25. Note that although the authors interpret this reduction in site discrimination as arising from a lowering of the long range ordering, such behavior is exactly that which would be expected for an alloy in its most fully ordered state, if Nb is the partitioning element. In that case, the sublattice composition would be $[Ti_{25}Nb_{25}][Al_{15}Nb_{35}]$; the combination of the 15 Al atoms with the 10 extra Nb atoms on the 'Al' sublattice would be expected to compensate the 25 Ti atoms, which have an intermediate elastic scattering power ($f_{Al} \ll f_{Ti} \ll f_{Nb}$). In this case, the ALCHEMI experiments would not be measuring site distributions at all, but rather the effects of ionization delocalization, as outlined in the next section.

Ionization delocalization

Ionization delocalization is the term coined to describe the experimental observation that different elemental excitations (e.g., Ni-K, Al-K, etc.) respond differently to the channeled electron intensity, with lower energy excitations generally responding less strongly to the channeling [5,6]. The lower response to the channeling of the soft Al-K X-rays relative to the medium energy X-rays, such as Ni-K, was responsible for the failure of the original formulation of ALCHEMI for analyzing ordered aluminide intermetallics, and sometimes resulted in "nonphysical" site-distributions [5,7]. For example, the analysis of $L1_2$-ordered $Ni_{76}Al_{21}Hf_3$ with the original formulation of ALCHEMI yielded the fraction of Hf alloying element on the 'Al' sublattice to be $p_{Hf'Al'} = -127\%$ [20]. Reanalysis of the same data with the "statistical" ALCHEMI formulation [3,4], which did not explicitly account for ionization delocalization but claimed to reduce its effect intrinsically, was no better, resulting in $p_{Hf'Al'} = -220\pm190\%$. Analysis of these same data with our formulation of ALCHEMI [10], which explicitly accounts for ionization delocalization, yields $p_{Hf'Al'} = 80\pm25\%$ [20]. While this result is consistent with the results of atom probe studies of similar alloys, which yielded $p_{Hf'Al'} = 76.9\pm8.3\%$ for $Ni_{76}Al_{23.5}Hf_{0.5}$ and $p_{Hf'Al'} = 84.4\pm3.5\%$ for $Ni_{76}Al_{23}Hf_1$, the poor statistical precision of the site-distribution suggested that the specimen be reanalyzed at more carefully chosen channeling conditions. Two independent analyses at the (200) systematic row and the [111] zone axis yielded $p_{Hf'Al'} = 76.9\pm6.6\%$ and $p_{Hf'Al'} = 78.0\pm4.3\%$, in excellent agreement with one another and consistent with the atom probe measurements.

For the data acquired from $Ni_{76}Al_{21}Hf_3$ at [111], the responses of the Ni, Al and Hf to the electron channeling are shown in Figure 2, both (a) uncorrected and (b) corrected for ionization delocalization. Note that the data are identical except that in Fig. 2b the channeling response (r_X - 1) for each element X has been multiplied by a "delocalization correction constant", L_{NiX}. Thus delocalization correction is accomplished with a single linear correction coefficient for each element. The superposition of the responses of the three elements in Fig. 2b for all orientations except those very near the zone axis is consistent with the fact that the {110}-type superlattice reflections are strongly excited only when the specimen is oriented to within a fraction of a degree of [111]. At orientations further from the zone axis, only fundamental (fcc allowed) reflections contribute to the channeling, and hence no discrimination between the sublattices is possible, as

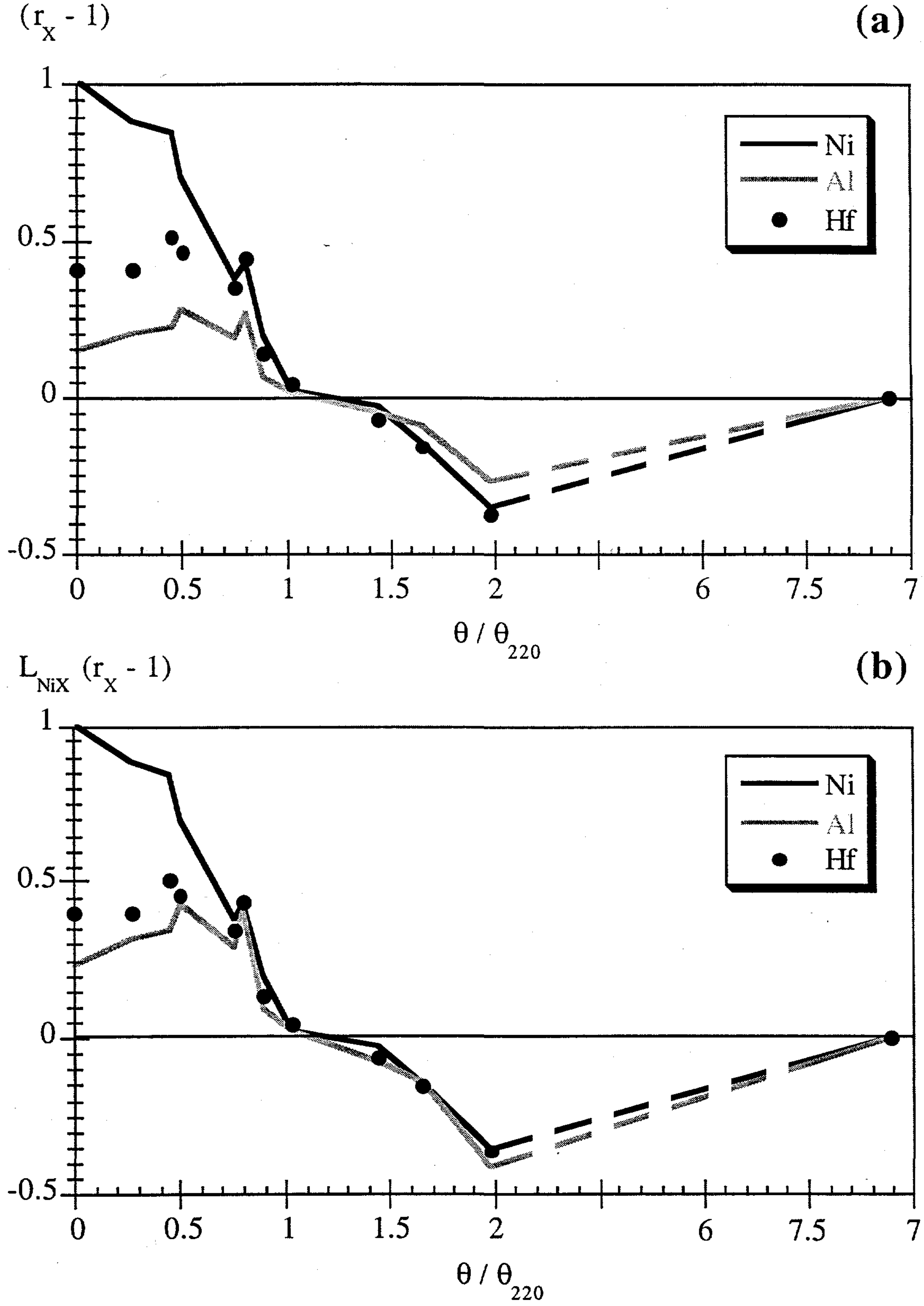


Fig. 2. Plots of channeling response $(r_X - 1)$ of the host and alloying elements X = {Ni, Al, Hf} (a) without and (b) with ionization delocalization correction factors L_{NiX} for $L1_2$-ordered (A_3B) $Ni_{76}Al_{21}Hf_3$ near [111]. The angular deviation from [111] is normalized to the Bragg angle of a (220) reflection. The superposition of the responses in (b) for $\theta / \theta_{220} > 0.5$ arises because no (110) superlattice reflections are strongly excited. Without delocalization correction (Fig. 2a), the similar delocalization behavior of Hf and Ni may be mistaken for a greater 'Ni' site preference.

discussed in the previous section. Note that if ionization delocalization were ignored, the similar responses (localization constants) of the medium energy Ni-K and Hf-L lines to the channeling, as shown in Fig. 2a, would be misinterpreted as Hf having a greater 'Ni' sublattice preference.

Several ALCHEMI formulations, which use both the "statistical" method [8,10] and the original "ratio" method of analysis [21], now incorporate explicit ionization delocalization correction. However, some recent ALCHEMI formulations do not incorporate ionization delocalization corrections [14,15], including the "ordered tie-line" (OTL) method [15]. Applying the OTL method, which can be viewed as representative of ALCHEMI formulations without ionization delocalization corrections, to the data acquired from the $L1_2$-ordered $Ni_{76}Al_{21}Hf_3$ alloy at [111] yields $p_{Hf'Al'}$ = 55.9%; for the data acquired at (200), where site-discrimination is poorer and hence the effects of delocalization more dominant, the OTL site occupancy is $p_{Hf'Al'}$ = 41.9%. The results acquired with OTL differ from one another by 14% and from the results established by both atom probe and ALCHEMI with delocalization correction by 20 - 35%. The significant difference between the predicted ordering behavior arises solely because the OTL method, neglecting ionization delocalization, misinterprets the differences in element responses arising from ionization delocalization as arising from differences in site occupancy. This point is made more dramatically by an OTL analysis of B2-ordered $Ni_{50}Al_{40}Fe_{10}$ at the (110) systematic orientation, where there is no superlattice reflection and hence no ability to discriminate between the sites. The OTL method yields $p_{Fe'Ni'}$ = 83%, consistent with Fe being chemically equivalent to Ni. This result is opposite to the actual ordering behavior (ALCHEMI with delocalization correction at (200) yields $p_{Fe'Ni'}$ = 23.7±0.9%) and can be easily explained by the trend in ionization delocalization ($L_{Al} \ll L_{Fe} \sim L_{Ni}$). Granted, this is an extreme example, since no site discrimination is even expected for B2-ordered alloys at (110). However, the site-discrimination is similar to that which would be expected at (200) if the (100) superlattice reflection is weak, as for the case of the Nb-15Al-25Ti alloy.

In short, ALCHEMI formulations that do not explicitly account for ionization delocalization cannot be expected to yield accurate site occupancies for aluminide intermetallic alloys. It should be noted that most of the ALCHEMI data found in the literature do not correct for ionization delocalization and cannot be assumed to be reliable.

Intrinsic alloy disorder

One of the shortcomings of ALCHEMI analysis is that one does not explicitly measure site-occupancies, but rather the degree of correlation among the sublattice occupancies of the host and alloying elements. The result is that the site-occupancies determined with ALCHEMI are always contingent upon an assumption about the state of order of the host elements. However, there is substantial evidence that for many common ordered intermetallic alloys, at least one of the host elements occupies only one of the available sublattices, to within the precision of ALCHEMI measurements (typically ~1%).

As an example, consider the results of a systematic study of 3d-transition metal doped iron aluminides $Fe_{50}Al_{45}Me_5$ [11], with Me = {Ti, V, Cr, Mn, Co, Ni, Cu}, which are shown in

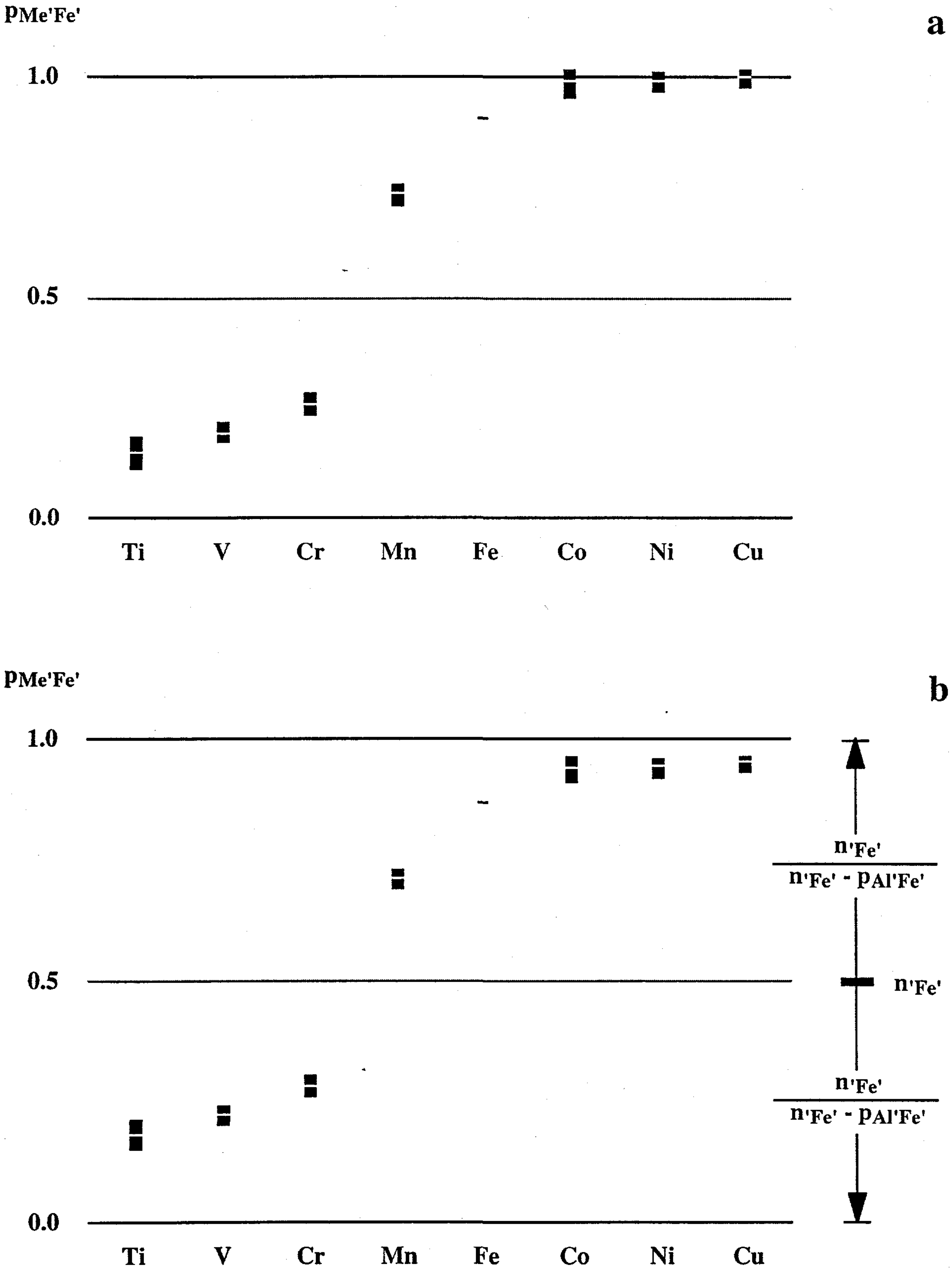
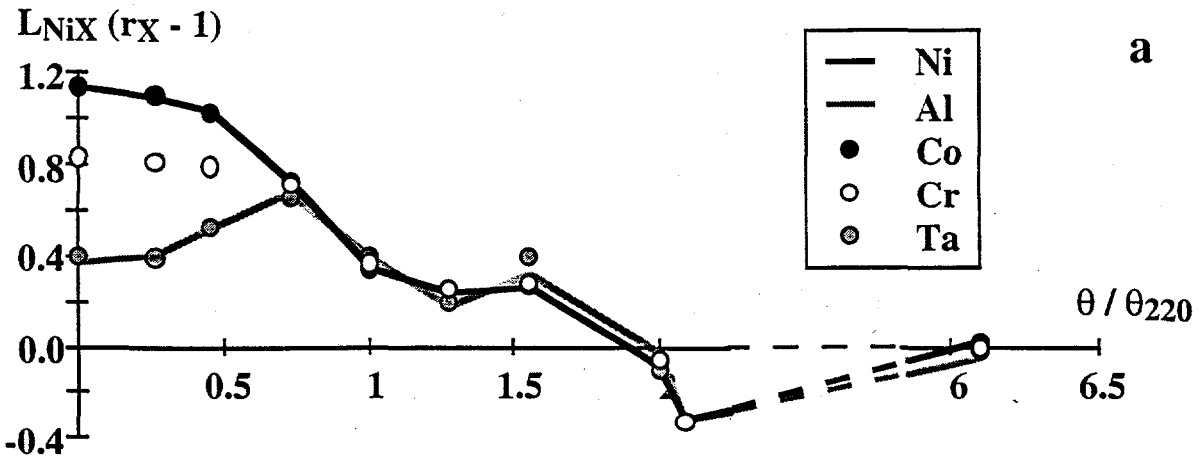


Fig. 3. Plot of the site occupancies of 3d-transition metals Me in B2-ordered $Fe_{50}Al_{45}Me_5$ (a) assuming negligible Al antisite defects and (b) assuming 5% of the Al sits on the 'Fe' sublattice ($p_{Al'Fe'} = 0.05$). The site fraction of the 'Fe' sublattice is $n_{'Fe'} = 0.5$. The 100% 'Fe'-site occupancy of elements Co, Ni, and Cu to the right of Fe in the periodic table is more consistent with the thermodynamic and kinetic models that explain these site occupancies and is consistent with other measurements that indicate that at least one of the host elements occupies its sublattice exclusively in many ordered intermetallic alloys.

Figure 3. For FeAl, the energy of formation for $Al_{'Fe'}$ (i.e., Al on the 'Fe' sublattice) antisite defects has been reported to be of similar magnitude to that for 'Fe'-site vacancies [22]; hence there is a real possibility that the ternary iron aluminides would exhibit some intrinsic disorder. The site-distributions consistent with the Al host element exclusively occupying the 'Al' sublattice are shown in Fig. 3a. Given this assumption, the alloying elements to the right of the Fe host element in the periodic table are seen, to within the precision of the measurement, to occupy the 'Fe' sublattice exclusively, displacing 10% of the Fe host element to the 'Al' sublattice. Corresponding site-occupancies consistent with 5% of the Al on the 'Fe' sublattice as antisite defects are shown in Fig. 3b. The assumption of intrinsic disorder essentially "compresses" the values of the site-occupancies nearer to the condition of random sublattice occupancy (50% for B2-ordered alloys). In particular, the site-occupancies of the elements to the right of Fe now appear to tend to a constant value of the site-occupancy less than 100%, here 95%. However, the 100% 'Fe' sublattice occupancy of Co, Ni and Cu is consistent with the strong 'Fe'-site preference of these elements and the rapid kinetics of the site-equilibration mechanism for alloying elements having an 'Fe'-site preference [11]. For this case, therefore, the exclusive 'Fe' sublattice occupancy for Co, Ni, and Cu is the most plausible alternative, and thus no substantial $Al_{'Fe'}$ antisite defect concentration is indicated. For more strongly ordered alloys with the B2 structure (e.g., NiAl), intrinsic disorder is exponentially less likely, since the energy of formation of an $Al_{'Ni'}$ antisite defect is much larger.

As a second example, consider an ALCHEMI analysis of a γ' particle in a René 95 Ni-base superalloy, with seven substitutional alloying additions: Ti, V, Cr, Co, Nb, Mo, Ta [23]. The two-phase submicrometer-scale microstructure makes this alloy an open system - there is no need for constitutional point defects since, for example, any $Ni_{'Al'}$ antisite defects could be eliminated by transformation of unit cells of the γ' to the γ phase. A plot of the channeling response of the Ni and Al host elements and three of the alloying elements is shown in Figure 4a. Assuming there are no appreciable antisite defects of either host element, these results are consistent with Ni and Co occupying the 'Ni' sublattice exclusively, Al and Ta occupying the 'Al' sublattice exclusively, and Cr partitioning between the two sublattices. If there were Ni anti-site defects on the 'Al' sublattice, an identical fraction of the Co alloying element would need to occupy the 'Al' sublattice as well in order to be consistent with the ALCHEMI measurement. Similar arguments hold for Ta and Al if Al antisite defects were present. On the whole, the alternative that the host elements have exclusive site occupancies is once again more plausible. A plot of the site occupancies of all alloying elements is shown in Figure 4b. Note the similarity with Fig. 3a in the trends in site-occupancy across the periodic table. Trends are also evident for elements within the same column of the periodic table.

These ALCHEMI measurements suggest that the intrinsic disorder of the alloys is smaller than that which would be necessary in order to influence the measured site occupancies (~1%). Intrinsic disorder on a smaller scale does not appreciably influence the measured site-occupancies, and cannot be ruled out on the basis of these measurements.



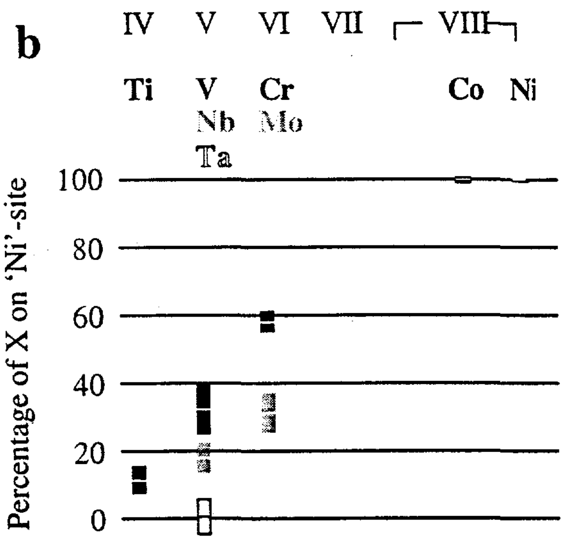


Fig. 4. (a) Plot of delocalization-corrected channeling responses for elements in an $L1_2$-ordered gamma prime particle of a René 95 superalloy. (b) The site occupancies of all detected alloying additions. Note that trends in the site occupancies are evident both across rows and down columns of the periodic table.

UNDERSTANDING THE PROPERTIES OF ORDERED INTERMETALLIC ALLOYS WITH ALCHEMI

From the first section of this paper, it is evident that many factors affect the accuracy and reliability of ALCHEMI measurements, but that very accurate site occupancies can be determined as long as these factors are properly heeded. The second section of this paper will explore the real materials science that can be explored using ALCHEMI. The usefulness of ALCHEMI in the development of intermetallic alloys is best seen in the context of systematic studies, where a family of related alloys are examined. Such studies can be used to establish trends in the site occupancies, which can help to explain other alloy properties that arise from the atomic-scale ordering behavior. The trends in the site occupancies can also help to establish the relative influence of thermodynamic and kinetic factors during alloy processing, which in turn strongly influence the properties of the resulting alloys.

Consider the systematic study of 3d-transition-metal doped B2-ordered $Fe_{50}Al_{45}Me_5$ [11], which was discussed in the previous section. The exclusive site-occupancies of the Co, Ni and Cu alloying elements can be explained in part by the strong (~2eV) site preferences of these alloying elements for the 'Fe' sublattice [24]. However, equally strong preferences are exhibited by elements Ti, V, and Cr for the 'Al' sublattice, which nevertheless exhibit substantial residual 'Fe' site occupancies. Therefore, thermodynamic factors alone cannot explain the ordering behavior. This discrepancy can be explained by considering the kinetics of the site-equilibration mechanism [11]. The exclusive site-occupancy of the late 3d transition metals can be explained because the site equilibration can occur whenever an 'Fe'-site vacancy is adjacent to an alloying element on the energetically unfavorable 'Al' sublattice (e.g., $Co_{'Al'}$). The kinetics of this equilibration are therefore limited by vacancy diffusion. However, site-equilibration of the early transition metals requires not only an 'Fe'-site vacancy and an alloying element on the energetically favorable 'Fe' sublattice (e.g., $Cr_{'Fe'}$), but also an Fe antisite defect ($Fe_{'Al'}$) on another adjacent site. The kinetics for the site equilibration of Ti, V, and Cr are therefore limited by diffusion of one of the two substitutional defects ($Cr_{'Fe'}$ or $Fe_{'Al'}$), which occurs over a longer time scale than the vacancy diffusion governing the site-equilibration of Cr, Ni and Cu. Therefore, the late transition metals have time to equilibrate, while the early transition metals do not.

The results of systematic ALCHEMI studies can also be used to explain observed changes in properties of ordered intermetallic alloys that depend on the underlying atomic-scale ordering of

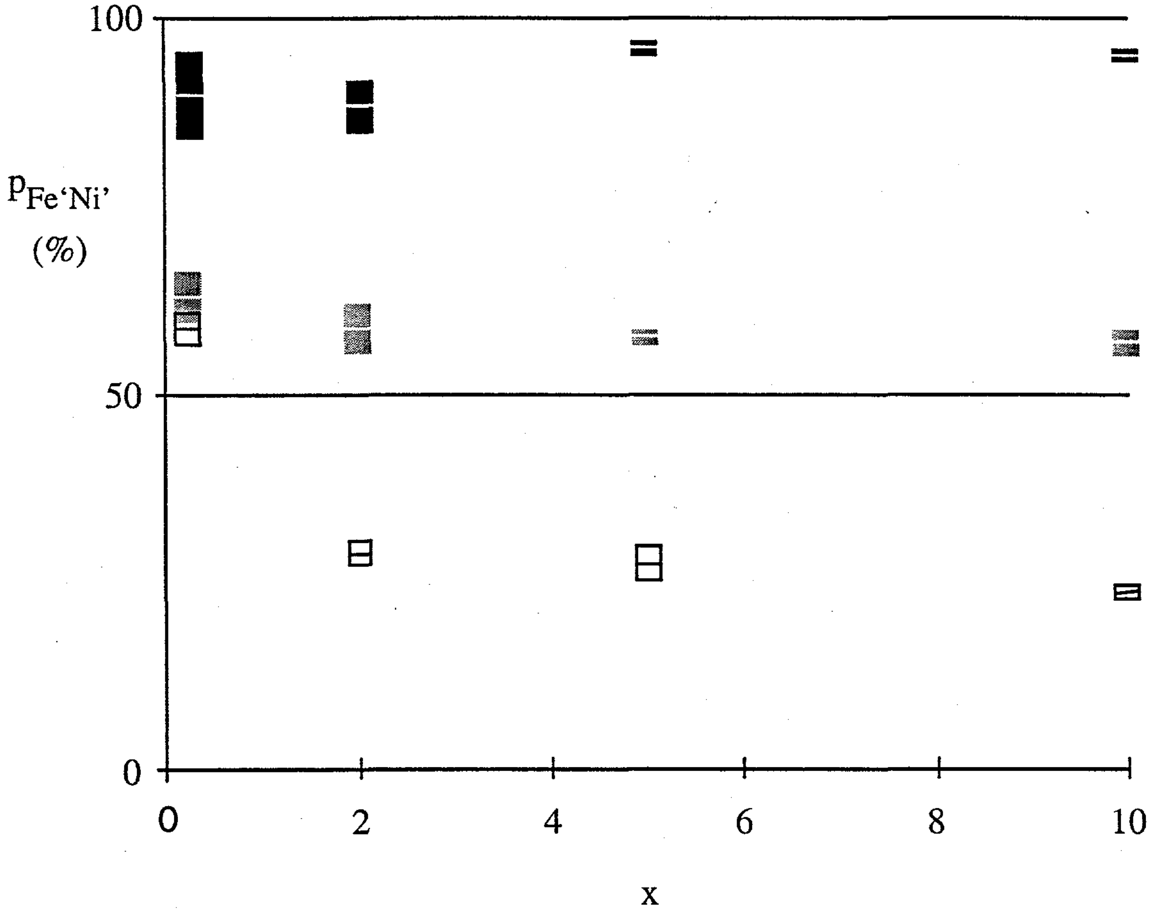


Fig. 5. Percentage of Fe occupying the 'Ni' sublattice ($p_{Fe'Ni'}$) as a function of the atomic percentage x of the Fe alloying element, for alloys of stoichiometry $Ni_{50-x}Al_{50}Fe_x$ (black), $Ni_{50}Al_{50-x}Fe_x$ (white), and $Ni_{50-x/2}Al_{50-x/2}Fe_x$ (gray).

the alloy. Consider, for example, a study that has been performed on a series of Fe-doped NiAl alloys [25,26]. Site-distributions are shown in Figure 5 for three series of alloys, with stoichiometries $Ni_{50-x}Al_{50}Fe_x$ (Ni-deficient), $Ni_{50}Al_{50-x}Fe_x$ (Al-deficient), and $Ni_{50-x/2}Al_{50-x/2}Fe_x$ (intermediate), and with four different alloying levels, x = 0.25, 2, 5, and 10. For the Ni-deficient alloys, ALCHEMI identifies a small residual 'Al'-site occupancy (~4 - 11%) for Fe. The smallest 'Al'-site occupancy in this series is exhibited by the alloy of composition $Ni_{45}Al_{50}Fe_5$, with measurements indicating that only 3.6±0.9% of the alloying element occupying the 'Al' sublattice. A residual 'Al'-site occupancy for all alloys in the Ni-deficient series is consistent with magnetic susceptibility and nuclear magnetic resonance (NMR) measurements on similar alloys [27]. For example, the measurement of local magnetic moments in these alloys is inconsistent with an exclusive 'Ni' site occupancy for the Fe alloying element. Note that it is only given the recent improvement in understanding of the factors influencing ALCHEMI that this small residual 'Al'-site occupancy can be identified as statistically distinct from exclusive 'Ni'-site occupancy for Fe. (For example, the systematic errors yielded by application of the ordered tie-line (OTL) method to the $L1_2$-ordered alloy in the previous section were an order of magnitude greater than the residual 'Al'-site occupancy that we have measured for $Ni_{45}Al_{50}Fe_5$.)

The ALCHEMI analysis of the Fe-doped NiAl alloys [26] also identifies a unique site-substitution behavior for an alloy that is within the composition range that Darolia et al. have reported as exhibiting enhanced ductility [28]. Enhanced ductility was reported for alloys in the Al-deficient series with alloying levels in the range $0.1 \leq x \leq 0.25$. As shown in Fig. 5, there is a sharp discontinuity in the Al-deficient series of alloys in the site distribution of the Fe at the 0.25% alloying level relative to the 2, 5 and 10% alloying levels, in contrast with little or no variation in the site distribution observed in the Ni-deficient and intermediate alloy series. The distinguishing characteristic of the site-substitution behavior of the Al-deficient alloy at the 0.25% alloying level is that there is more Ni than Fe on the 'Al' sublattice, which occurs for $p_{Fe'Ni'} >$ 50%. *Ab initio* calculations predict that configurational entropy is the factor most responsible for this dramatic change in the site-occupancy [24]; if this is the case, the fraction of Fe on the 'Ni' sublattice should increase as the concentration of the Fe drops below 0.25 at.%. The compositional range exhibiting enhanced ductility therefore correlates strongly with this "inversion" of the 'Al' sublattice concentrations of Ni and Fe. It is currently hypothesized that the increase in ductility results from the interaction of the alloying element with interstitial impurities [29], such as C [30]. However, this inversion of the Ni and Fe concentrations on the 'Al' sublattice may help to explain why the ductility enhancement has been observed only in a narrow range of compositions.

CONCLUSIONS

ALCHEMI is approaching the status of an established analytical technique, where accurate site-occupancies are routinely acquired from a variety of ordered intermetallic alloys. Precisions better than ±1% in the site occupancies have been achieved, and the results of ALCHEMI studies are now being used to explain other alloy properties. However, there is considerable variability in the theory and practice of ALCHEMI. The following factors influence the reliability of the ALCHEMI technique.

1) The preferred microanalysis standard for ALCHEMI is a spectrum acquired from the specimen itself at an orientation where channeling is negligible, as opposed to microanalysis k-factors. This "self-normalization" scheme avoids the systematic errors that are associated with X-ray microanalysis in the AEM.

2) A strongly excited superlattice reflection of the ordered alloy is necessary in order to obtain site discrimination between sublattices in an ordered intermetallic alloy. ALCHEMI cannot be used to extract the site occupancies when the elastic scattering powers of the alternating planes are similar, which can occur when the host elements are of similar atomic number or when the alternating planes compensate one another because the average elastic scattering powers of the host and alloying elements on these planes are similar.

3) ALCHEMI formulations that do not explicitly account for ionization delocalization cannot be expected to yield accurate site occupancies for aluminide intermetallic alloys. In particular, the ordered tie-line (OTL) method, which does not account for ionization delocalization, has been shown in cases to yield site occupancies with inaccuracies of 20% or higher.

4) Although the site occupancies determined with ALCHEMI are always contingent upon an assumption about the state of order of one of the host elements, there is substantial evidence that at least one of the host elements typically occupies its sublattice exclusively in many common ordered intermetallic alloys, including B2-ordered and $L1_2$-ordered aluminides.

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