

# The Effects of Boron Impurities on the Atomic Bonding and Electronic Structure of Ni<sub>3</sub>Al

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## INTRODUCTION

The intermetallic alloy nickel aluminide, Ni<sub>3</sub>Al, exhibits several unique physical and mechanical properties which make it attractive for potential use in a wide variety of technological applications.<sup>1</sup> Among these are its low density, high melting temperature, resistance to oxidation, and unlike most conventional metallic alloys, an increase in yield stress when exposed to increasing temperatures. Single crystals of Ni<sub>3</sub>Al are extremely ductile, a property not shared by polycrystalline forms of this alloy.<sup>2</sup> The brittleness observed in the disordered systems is believed to be due to intergranular fracture in the material. However, recent work involving the doping of boron impurity atoms has shown an increase in the ductility of this intermetallic system.<sup>3</sup> Doping 250 parts per million (ppm) of boron atoms increases the elongation of polycrystalline Ni<sub>3</sub>Al from a few percent to nearly fifty percent.<sup>4</sup>

To better understand the influence of boron doping on the mechanical properties of Ni<sub>3</sub>Al, we performed a study of the electronic structure and atomic bonding of boron with the nickel and aluminum atoms in this alloy using x-ray emission spectroscopy (SXES). It is believed that the increased ductility observed in the boron doped systems is due to interplanar metallic bonding between the nickel and boron atoms, and the sensitivity of SXES to the local bonding environment of the emitting atoms makes it an ideal tool for studying these systems.<sup>5,6</sup> This technique was used recently to obtain information about the structure of nickel compounds containing small amounts of sulfur.<sup>7</sup>

## EXPERIMENTAL AND CALCULATIONAL DETAILS

Preliminary measurements were made at Louisiana State University's Center for Advanced Microstructures and Devices (CAMD) utilizing the Tulane University-National Institute for Standards and Technology-University of Tennessee (TNT) soft x-ray fluorescence spectrometer. A detailed description of this instrument can be found elsewhere.<sup>13</sup> After these measurements were analyzed an in-depth set of measurements was obtained at Lawrence Berkeley National Laboratory's Advanced Light Source (ALS) at Beamline 8.0, employing the University of Tennessee at Knoxville's soft x-ray fluorescence (SXF) endstation. Photons with energies ranging from 180 to 220 eV, through the boron K absorption edge, were used to excite the samples.

All measurements reported here were made with a 100-micrometer entrance slit for the spectrometer. The spectra were obtained with a 1500 lines/mm, 10-meter radius grating. At the boron K edge the resolution of the spectrometer is approximately 0.8 eV. The energy resolution of the monochromator was set to 0.3 eV during most of these measurements. The boron K-valence emission spectra were calibrated with a reference sample of hexagonal boron nitride (h-BN).

The boron doped Ni<sub>3</sub>Al samples (nickel doped with 24.8% aluminum and 500 ppm of boron) were supplied by C. T. Liu, a materials scientist at Oak Ridge National Laboratory. The

alloys were prepared by arc melting and drop casting techniques, followed by various thermomechanical treatments.<sup>8</sup>

Electronic structure calculations for nickel-boron and nickel-aluminum-boron bonding systems were performed by Dr. Jan van Ek using the linear muffin-tin orbital method within the atomic sphere approximation (LMTO-ASA).<sup>9</sup> Exchange and correlation effects were treated within the local density approximation (LDA) of density functional theory.<sup>10</sup> Self-consistent solutions to the Kohn-Sham equations were obtained for all the electrons in the system using the exchange-correlation potentials as parameterized by von Barth and Hedin.<sup>11</sup>

## RESULTS AND DISCUSSION

Soft x-ray emission from the K(valence) bands in boron corresponds to the filling of core level holes by electrons from the valence band in these materials. Emission occurs when a photon, with enough energy to remove an electron from the 1s core level, creates a hole in the core which is then filled by an electron from the valence band. The filling of the hole results in the production of a photon that has an energy equal to the difference between core and valence band energies. Therefore, this technique is used to gain information about the boron valence bands in these materials. Additionally, SXES is sensitive to the nature of the chemical bonds, displaying marked differences in the energy distribution and fine structure of emission from elemental boron systems, chemical compounds containing boron, and transition metal boride materials.<sup>12-15</sup> Also, because the x-ray transitions are localized to the first coordination sphere of the emitting atom, XES is sensitive to short-range order (coordination number, bond lengths, etc.). All these factors make XES an invaluable tool for determining the surrounding environment and the local chemical bonding of boron impurity atoms in these intermetallic compounds.

The main difficulty in analyzing the boron K-valence XES in this boron doped system,  $\text{Ni}_3\text{Al:B}$ , is the absence of suitable reference samples whose boron spectra can be used as fingerprints for particular boron-nickel and boron-aluminum bonding. Therefore, we turned to the shape of the emission spectrum in order to understand the impurity bonding, and performed two electronic structure calculations for the  $\text{Ni}_3\text{Al:B}$  system, as shown in Figures 1a and 1b. The first calculation examines the nickel-boron bonding for a system of boron atoms occupying

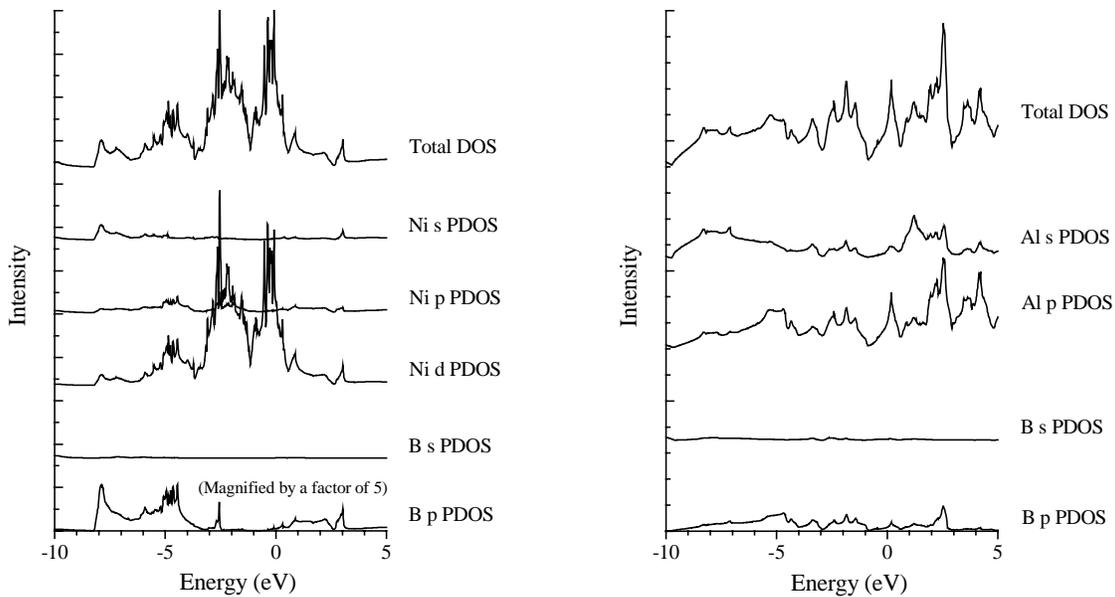


Figure 1. Total and partial density of states distributions for calculated boron  $\text{Ni}_3\text{Al:B}$  systems. Boron-nickel type bonding for boron atoms surrounded by six nickel atoms (a) and boron-aluminum type bonding for boron atoms surrounded by four nickel and two aluminum atoms (b).

nickel-rich octahedral interstitial regions (boron atom surrounded by six nickel atoms) in the alloy's structure. The second considers the aluminum-boron bonding for a system with boron atoms occupying a different octahedral interstitial site (boron atom surrounded by four nickel atoms and two aluminum atoms). Figure 2 illustrates these two possible boron atom locations within the  $\text{Ni}_3\text{Al}$  lattice. The six-fold nickel atom configuration corresponds to the boron atoms occupying octahedral site B1. The four nickel-two aluminum atom configuration corresponds to the boron atoms occupying octahedral sites B2. The calculations show that for nickel-boron bonding there is hybridization between the boron 2p and nickel 3d states, and for aluminum-boron bonding the hybridization is between the boron 2p and aluminum 3s and 3p states. In order to determine which type of bonding is taking place in the  $\text{Ni}_3\text{Al}:\text{B}$  system, thereby revealing the location of the boron atoms in the alloy, we compare an above threshold emission spectrum from the sample with the calculated boron 2p PDOS in Figure 3. The calculations have been broadened to account for the 0.5 eV experimental resolution of the spectrometer. The FWHM (5.1 eV) and shape of the emission from the sample is more consistent with the nickel-boron bonded system (4.5 eV), than with the aluminum-boron bonded system (6.8 eV). This comparison shows that the boron K(valence) emission measurements from the  $\text{Ni}_3\text{Al}:\text{B}$  samples are more consistent with boron impurity atoms occupying the nickel-rich octahedral interstitial sites. This conclusion is in agreement with the results of other theoretical calculations which state that the formation energy for a boron atom placed at a nickel rich octahedral interstitial site in  $\text{Ni}_3\text{Al}$  is -4.4 eV per unit cell, as opposed to a nickel deficient octahedral interstitial site which is only -0.08 eV per unit cell.<sup>16</sup> Analysis of the charge redistribution induced by the boron impurity atoms when placed at the nickel-rich interstitial sites shows that the boron atoms greatly enhance the observed interplanar ductility in  $\text{Ni}_3\text{Al}:\text{B}$ .<sup>16</sup> This suggests that the boron 2p-nickel 3d hybridization between nearest neighbor atoms is the mechanism for this enhancement.

## CONCLUSION

Measurements of boron K(valence) x-ray emission spectra of boron impurities in  $\text{Ni}_3\text{Al}$  (500 ppm boron) excited by tunable synchrotron radiation have been presented. These spectra are compared with electronic structure calculations of boron impurities in nickel-rich and nickel-deficient bonding systems. It appears that the boron impurity

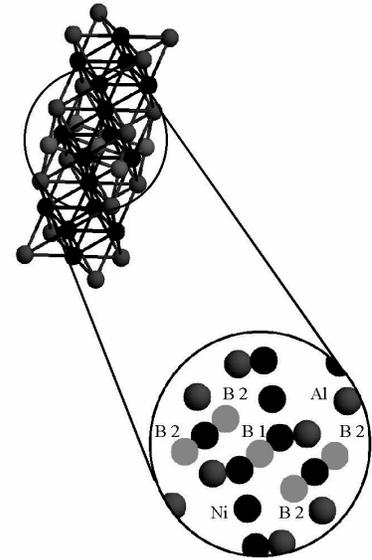


Figure 2. Illustration of the  $\text{Ni}_3\text{Al}$  lattice showing possible sites for boron impurity atoms.

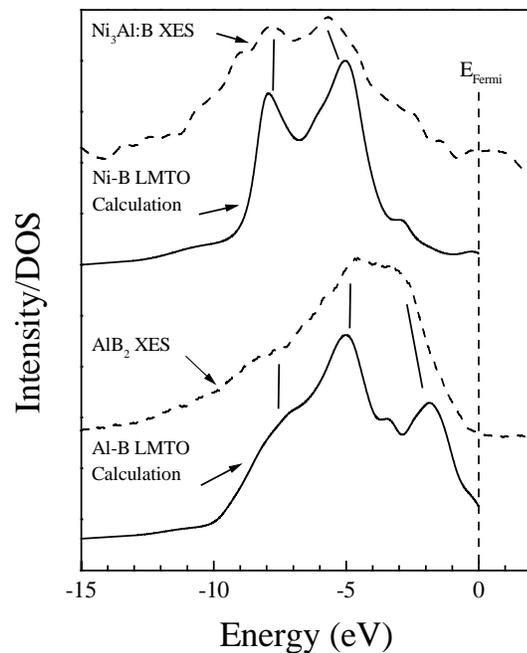


Figure 3. Boron 2p partial density of states distribution for the measured  $\text{Ni}_3\text{Al}:\text{B}$  system compared with calculated values for boron-nickel and boron aluminum type bonding.

atoms preferentially bond with nickel atoms in Ni<sub>3</sub>Al, and that boron 2p-nickel 3d hybridization takes place. It seems that the boron atoms prefer to occupy octahedral interstitial sites with six-fold nickel atom coordination. Together with electronic structure calculations, this suggests an enhancement of the interplanar metallic bonding between nickel atoms which results in an observed increase in ductility for boron doped Ni<sub>3</sub>Al alloys.

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