

X-Ray Absorption Near Edge Structure (XANES) Calculations for the Amorphous $\text{Fe}_{80}\text{B}_{20}$ - and $\text{Ni}_{80}\text{B}_{20}$ -Alloys

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Xanes spectra of the amorphous $\text{Fe}_{80}\text{B}_{20}$ - and $\text{Ni}_{80}\text{B}_{20}$ -alloys have been investigated using the electron multiple scattering theory of Durham et al. The calculations were based on several models for the structure of amorphous $\text{Fe}_{80}\text{B}_{20}$ and $\text{Ni}_{80}\text{B}_{20}$. Very good agreement between theoretical and experimental XANES curves was met. Opposite to former expectations for obtaining information on bond angles by XANES, this study shows that XANES points to more complex features of the structure than can be expressed in terms of bond angles.

1. Introduction

The most detailed information about the structure of the binary amorphous alloys $\text{Fe}_{80}\text{B}_{20}$ and $\text{Ni}_{81}\text{B}_{19}$ up to now is contained in the partial pair correlation functions, which can be obtained by diffraction techniques using contrast variance methods such as isotopic substitution [1, 2]. These functions yield the atomic distances and the partial coordination numbers. Basing on these data several authors successfully have constructed three-dimensional structural models for these alloys.

For a better understanding of the structure of an amorphous system information about higher order correlation functions is desirable [3, 4], such as bond angle distributions [5, 6].

It has been shown that a XANES-spectrum is determined to a certain extent by the bond angles of the investigated atomic arrangement [7–9]. However, in contrast to diffraction techniques, there is no straightforward way from experimental XANES data to any structural information. Therefore evaluation goes an indirect way: Starting from a trial structure the theoretical XANES-curve is simulated and compared to the experimental one. Depending on the agreement between both curves the trial structure is accepted or rejected. Usually the trial structure fulfills structural properties which have been obtained from other methods. In the case of an amorphous alloy this means that the structural models are limited by the

necessity of dense filling of space with atoms of a finite size together with the experimentally known pair correlation functions. In the present case of the amorphous alloys $\text{Fe}_{80}\text{B}_{20}$ and $\text{Ni}_{81}\text{B}_{19}$ it is a perfectly tailored task for a XANES investigation to distinguish between several structural models which are almost identical regarding the pair correlation functions and only different regarding higher order correlation functions.

2. Structural Models for the Amorphous $\text{Fe}_{80}\text{B}_{20}$ -Alloy

For the present investigation several structural models for the amorphous alloy $\text{Fe}_{80}\text{B}_{20}$ are used. The structural models originate from the works of Fujiwara [10], Brandt [11], Zweck [12, 13], Dubois [14], and Beyer [15]. The models of Dubois and Beyer originally had been set up for the amorphous alloy $\text{Ni}_{81}\text{B}_{19}$, not for $\text{Fe}_{80}\text{B}_{20}$. Since the experimentally determined pair correlation functions for $\text{Fe}_{80}\text{B}_{20}$ and $\text{Ni}_{81}\text{B}_{19}$ are quite similar, the models for $\text{Ni}_{81}\text{B}_{19}$ tentatively are utilized for $\text{Fe}_{80}\text{B}_{20}$, too. The partial pair correlation functions, which can be calculated from the models' atomic coordinates, agree well with the experimentally determined ones as far as the general features are considered [16].

A model showing an intentional bad agreement with the diffraction data was also used for the purpose of testing the sensitivity of the method. It is named "test model" in the following. The essential discrepancy between this test model and the experimental data is that the partial Fe–Fe-distance is too large, whereas its Fe–B-distance agrees well with the experimental data.

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The properties of the structural models for Fe₈₀B₂₀ and Ni₈₁B₁₉ have been discussed in detail in a foregoing paper [16]. From the large amount of structural properties investigated in [16] only the basic observations will be repeated here:

Surprisingly, most of the bond angle distribution functions in the models cited above as well as their pair correlation functions are almost identical among each other.

Therefore there seems to be little need to try to determine the bond angle distributions in an amorphous alloy, since they arise already from the geometrical necessity of dense filling of space. From this point of view there would not be any motivation further to carry out a XANES investigation. However, nevertheless differences can show up among the XANES spectra as obtained from these almost identical models. It has been shown [8, 9, 17, 18] that a XANES spectrum is not only sensitive to angular correlations or to simple atomic distances but depends also on the mutual distances within those atomic triplets which are arranged roughly on straight lines. Therefore XANES cannot be regarded as just a tool to evaluate bond angles. Instead of this we have to consider also more complex characteristics of the structure.

3. First XANES Investigation for an Amorphous Alloy

The first XANES calculations for an amorphous alloy have been performed by Gaskell *et al.* for amorphous Pd–Ge [19]. In this study several polyhedra had been set up as trial models for the short range order and as an input for the simulation of the XANES curve. For two reasons, however, this way seems to have reached its limits:

I) a general experience from XANES-studies is that at least three, better more shells of atoms around the absorbing central atom are required for a good calculation of a XANES-curve [20]. It is necessary for the electron multiple scattering calculation to have all these shells involved in the calculation in order to obtain a correct result. This rule seems to be more important for highly symmetric clusters than for less symmetric ones. Therefore the calculated XANES-curve of a small trial cluster is not representative for the real extended structure in which the cluster is embedded.

II) numerical analysis of structural models of amorphous alloys has not yielded any evidence for a “typi-

cal” “average” short range order in the structure. Even the number of atoms within the first coordination sphere varies around an average value from atom to atom [16, 21, 22]. According to the structural models it may be stated that each possible (X-ray absorbing) central atom has an individual short range order: An individual distribution of partial distances, of partial bond angles and individual partial coordination numbers. Classification of all these individual short range orders into few categories is perhaps possible but must be done very carefully. Generally, an experimental XANES curve will have to be considered as a sum of contributions of different atomic sites. Therefore the relation between a XANES curve and just one model for the short range order is questionable.

4. Present Strategy for XANES Calculations for an Amorphous Alloy

Based on the insight into the structure as developed in the foregoing chapters the following strategy for a XANES evaluation was set up:

1st step: Get for the amorphous alloy under consideration a structural model which is a set of cartesian coordinates of typically 1500 to 2000 atoms within the limits of a cube or a sphere.

2nd step: Make a random choice of 40 to 50 central atoms of the desired chemical element. Since the XANES calculations require a spherical cluster of atoms within the radius of 0.55 nm around the central atom, only such central atoms with a distance of at least 0.55 nm away from the surface of the model could be accepted for the calculations. The number of 40 to 50 central atoms was found to be a good compromise between the convergency of the results and the available computer resources. The amount of computer time required for the calculation of a XANES-spectrum for each central atom is appreciable. As a thumb rule: The XANES calculation for one central atom takes 15 minutes of CRAY time.

3rd step: Set up the coordinates of each cluster of atoms surrounding each of the selected central atoms. The radius of the cluster is restricted to approximately 0.55 nm. This radius coincides roughly with a minimum in the partial metal-metal pair correlation function.

4th step: Calculate the XANES-spectrum for each of these central atoms with its surrounding cluster.

5th step: The average of all these individual results is the total XANES result for the actual structural model and may be compared to an experimental curve.

5. Preparation of Samples and Performing the XANES Measurements

For the X-ray absorption measurements the following samples were prepared: $\text{Fe}_{80}\text{B}_{20}$: prepared by planar flow cast technique. The sample was purchased from Allied Chemical Corp. as Metglas 2605. The sample was thinned to its optimum thickness for XAS measurements with a RF sputtering machine operated in the etching mode.

$\text{Ni}_{80}\text{B}_{20}$: This sample was produced in a thickness of 6 μm by RF-sputtering onto Mylar foil. After sputtering the sample was checked for being amorphous by X-ray diffraction.

Auger electron spectroscopy of the sample revealed a contamination by carbon of several atomic percent, but this was shown to be of little impact on the short range structure in general.

The measurements at the Fe- and Ni-K-edges were performed at liquid nitrogen temperature in transmission mode at the working station ROEMO 2 at the synchrotron radiation laboratory of HASYLAB at DESY. The double crystal monochromator was equipped with Si(311) crystals and exhibits an energy resolution of $\Delta E < 1$ eV. The spectra could be recorded with very good signal to noise ratio with a measuring time of 2 seconds per energy step.

6. Tools for the XANES Calculation

XANES calculations require a set of scattering phase shifts for the atomic species involved. In the present case this set was generated with the program MUF POT developed by Pendry and co-workers [23, 24], which uses Hartree Fock wave functions as input [25] together with the coordinates of the unit cell of a crystalline reference compound with similar stoichiometrical composition in the ideal case. In the present case the crystalline alloy Fe_2B served as a reference compound [26].

The input data for the XANES program [27] are the following:

I) Scattering phase shifts as calculated with the program MUF POT.

II) Coordinates of the atoms centered around the X-ray absorbing atomic sites.

III) Transition matrix elements for the free atom case. This term contains no oscillating structure and only determines the weak overall slope of the result. The data for iron atoms were kindly provided by P. J. Durham.

In the present investigation an updated version of the XANES program was used [28]. Among its several advantages the most interesting feature for the present study is the facility to switch off certain multiple scattering paths [28, 29]. If all multiple scattering events are switched off, even a curved wave single scattering calculation can be run. Making use of these features, the importance of the single- and the several multiple scattering processes can be studied in detail. Moreover, to omit unimportant scattering processes saves computer time.

Before the calculation of XANES for the amorphous case, the procedure was checked using the less complicated example of crystalline Fe_2B . The XANES calculation for crystalline Fe_2B is discussed in more detail in [8, 9]. For the calculation of the crystalline case the following parameters were used:

Radius of the cluster of atoms around central atomic sites: 0.55 nm.

Maximum angular momentum included in the atomic phase shifts: $\text{LMAX} = 3$.

Maximum angular momentum included in the symmetrized single centre expansion: $\text{LOUT} = 10$.

Restriction of multiple scattering: Full multiple scattering is performed for atoms within a radius of less than 0.41 nm. Beyond this radius only intershell multiple scattering (definition: see [28] and [29]) together with single scattering is performed because the contribution of the intrashell multiple processes can be neglected for these atoms. This partly restricted XANES calculation nevertheless will be named "full multiple scattering" for simplicity.

Having these parameters and the phase shifts confirmed for crystalline Fe_2B , the same phase shifts as well as the same parameters for the calculation were used for the XANES calculation with "amorphous" neighbourhoods.

7. XANES calculations for the Structural Models

According to the 4th step of the strategy as sketched in chapter 4 the XANES spectra have to be calculated

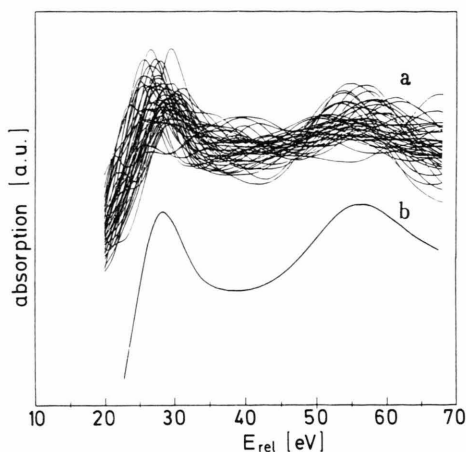


Fig. 1. XANES-spectra for one structural model (Fujiwara). a) Thirty spectra each for one individual atomic surrounding; b) Average of the curves shown in a).

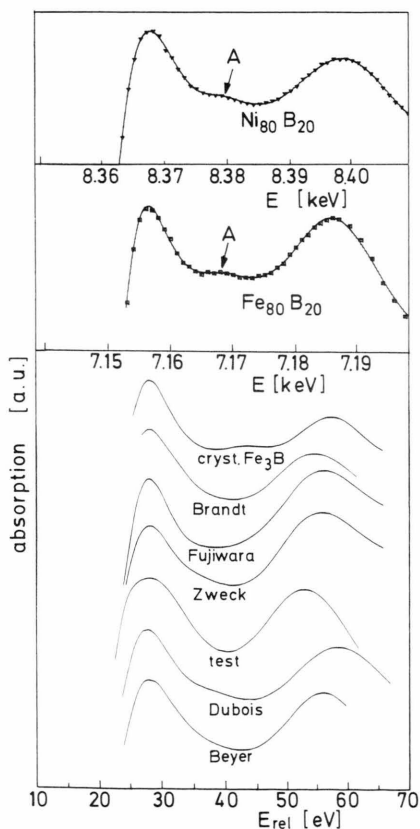


Fig. 2. Amorphous $\text{Fe}_{80}\text{B}_{20}$ and $\text{Ni}_{80}\text{B}_{20}$; comparison of experimental and calculated ($\text{Ni}_{80}\text{B}_{20}$) XANES spectra; calculations with full multiple scattering.

for a selection of 40 to 50 central atoms. Figure 1 shows 30 of the individual XANES results for the Fujiwara model. Regarding this plot it may seem daring to treat the average of these various curves as a result for the model in total. However, it was found that the characteristic shape of the final sum curve could already be seen after the averaging of some 15–20 of these individual results. To increase the number to 40–50 makes the result still more reliable.

Figure 2 shows the results for the six structural models, together with the experimental curves for $\text{Fe}_{80}\text{B}_{20}$ and $\text{Ni}_{80}\text{B}_{20}$.

We note that the general features of the experimental curves are also represented by the model calculations. However, the details of the curves for the models are different. The results for the Zweck- and the Dubois-models exhibit a bend around 35 eV to a less steep slope down to the minimum, which is located above 42 eV. This feature can be related to the small peaks in the experimental curves which are marked by "A". The result for crystalline Fe_3B in b.c.t. structure [26, 30, 31] also exhibits a small peak between the two main peaks, but its energetic location is significantly too high. Opposite to the shape of the Zweck- and the Dubois-models the result for the Fujiwara model contains a rather sharp peak at the edge, followed by a pronounced minimum below 40 eV.

The shape of the curves for the Brandt- and the Beyer-models as compared to the other ones show a pronounced minimum above 40 eV without any indication of a convex run in the energy range around A. The result for the test model agrees much worse with the experimental curves than all other results. This illustrates that a wrong trial structure leads to a significantly bad calculated XANES curve. Out of these results the shapes of those for the Zweck- and the Dubois-model coincide more than the others with the experimental data.

In order to find out the reasons for the differences among the curves the calculations were performed again under certain restrictions. The first variant for the calculation was to perform it without any multiple scattering processes i.e. only with curved wave single scattering. In this case a XANES curve is determined only by the radial arrangement around the atomic sites. The results for the calculations are shown in Figure 3. Now we recognize that the shapes of all the curves with the exception of the Brandt-model are almost identical, even for the less realistic test model. This agrees with the fact that the radial pair distribu-

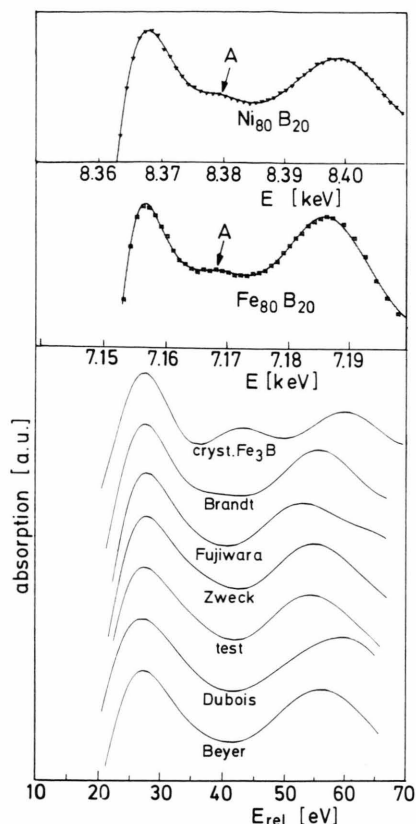


Fig. 3. Amorphous $\text{Fe}_{80}\text{B}_{20}$ and $\text{Ni}_{81}\text{B}_{19}$; Comparison of experimental and calculated XANES spectra; calculations with curved wave single scattering.

tions of the different structural models also are very similar. In addition, these results show that the differences between the results in Fig. 2 between $E = 25$ eV and 45 eV in fact originate from multiple scattering. These differences therefore point to differences between the structural models, which depend rather on higher order correlations than on pairwise correlations.

Figure 3 shows also that the second peak around 55 eV for the Beyer- and even more for the Dubois-model is located at a higher energy than for the other models. A radial contraction of the atomic cluster leads to an expansion of the periodicity of a XANES-result [8, 9, 17, 18]. Therefore, the different location of the "55 eV-peak" is explained by the fact that in these two models, which had been constructed for amorphous $\text{Ni}_{81}\text{B}_{19}$ according to the diffraction data [2], the atomic distances are shorter than in $\text{Fe}_{80}\text{B}_{20}$ [1]. This difference in the periodicity of the XANES curve

is also visible from the experimental curves for the $\text{Ni}_{80}\text{B}_{20}$ - and $\text{Fe}_{80}\text{B}_{20}$ -alloys.

In a next step the calculations were performed again with full multiple scattering, but now omitting the boron atoms from the structural models. In this case, again, within the range between 25 and 38 eV identical XANES curves were obtained, even for the test model [9]. Therefore the different runs of the curves in Fig. 2 do not arise from any differences between higher order correlations of the *metal* atoms, but from the question, how the *boron* atoms are located relative to the metal atoms. Note that the test model differs from the other models essentially regarding the bad relation between the metal-boron and the metal-metal partial distances.

Conclusions

Having discussed in detail the results, the following can be concluded:

- The concept of XANES calculations for a set of individual short range orders, together with the reliable XANES-theory, leads to a good agreement between theoretical and experimental curves.
- As for the main features, the XANES-results for all the discussed realistic models agree well with experimental data.
- Differences among the results originate from higher order correlations between metal- and boron atoms.
- The short range structures in the $\text{Fe}_{80}\text{B}_{20}$ - and the $\text{Ni}_{80}\text{B}_{20}$ alloys seem to be very similar, irrespective of slight differences in the mean atomic distances [1, 2].
- Finally, the experimental data suggest that the model of Dubois [14] under this point of view is the most adequate one.

Due to the complex structure of an amorphous solid and its large variety of individual atomic short range orders, at the present state of knowledge it does not seem to be possible to deduce any of these calculated curves from simple, obvious structural elements.

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