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X-RAY ABSORPTION MEASUREMENTS AT THE BORON K-EDGE WITH AMORPHOUS IRON- AND NICKEL-BORON ALLOYS

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Abstract - X-ray absorption spectra from the K-edge of boron in amorphous and crystallized $\text{Fe}_{80}\text{B}_{20}$ alloys are presented. The spectra are discussed together with calculated densities of states, a possible core-exciton energy level and basic XANES phenomena. Satisfying coincidence between band structure calculations and experimental results can be recognized. The results in principle permit to decide between different models for the atomic structure of the amorphous $\text{Fe}_{80}\text{B}_{20}$ alloy. The structure model of Zweck rather approaches the present experimental data than the model of Fujiwara.

I - INTRODUCTION

Among the binary amorphous alloys one of the most intensively studied one is $\text{Fe}_{80}\text{B}_{20}$. Its preparation conditions, its crystallization behaviour, its atomic structure, its modelling, and its electronic properties have been thoroughly studied. Latest progress in performing band structure calculations to amorphous solids was applied to $\text{Fe}_{80}\text{B}_{20}$ /1/. EXAFS- and XANES-studies of the Fe-K-edge in amorphous and crystallized $\text{Fe}_{80}\text{B}_{20}$ have already been published /2,3,4/ and fulfilled their aim to give information about the vicinity of the absorbing atom, in this case the iron atom. Since there is strong interest on XAS-data of the atoms of all components present in the corresponding alloys, the present first study of boron-absorption in alloys was carried out /5,6/.

II - EXPERIMENTAL SET-UP

The measurements have been performed at the Berlin synchrotron radiation facility BESSY. The beamline was equipped with the plane grating monochromator SX-700 /7/, which covers an energy range from 9 eV to 2200 eV. Its energy resolution depends from the size of the exit slit and from that area of the diffracting elements, which is exposed to the radiation /8/. Maximum energy resolution to be achieved at $E=200$ eV is $\Delta E=0.1$ eV. For the present measurements, however, in most cases a tuning with ΔE approximately 0.2 eV was utilized in order to maintain higher photon flux. The absorption spectra were taken with the transmission arrangement shown in figure 1.

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Fig.1. Experimental set-up for absorption measurements

All components were contained within an ultrahigh-vacuum system not shown in fig. 1. The incident monochromatic beam released electrons from a gold mesh, which were detected by a channel electron multiplier (CEM, type GALILEO 4700) to provide the measure for the intensity I_0 . Behind the gold mesh the beam transmitted the sample, which could be cooled to liquid nitrogen temperature. Behind the sample the beam hit a gold-covered plate, whose electron-yield, detected by a second channeltron of the same type, yielded the signal for the intensity I_1 . Thus the absorption coefficient was obtained as

$$\mu(E) = \ln(I_0/I_1) \quad (1)$$

The spectra were taken with energy steps of 0.1 eV. In spite of the high sweep rate of usually 3 seconds/energy step in many cases no splinefit was necessary during data evaluation because of the very high photon flux. For the same reason both channeltrons were operated in the current mode. Before measuring, different tests were made to verify the calibration of the instrument and to ensure that no distortions occurred in the energy range of interest.

III - PREPARATION OF THE SAMPLES

According to absorption coefficients for the energy of the B-K-edge /9,10/ a suitable thickness for the specimens of approximately 100 nm was calculated. Thin films of alloys and of boron were then prepared by RF-sputtering from molten sputter targets of the desired composition. The compounds chosen were $\text{Fe}_{80}\text{B}_{20}$, $\text{Fe}_{83}\text{B}_{17}$, $\text{Fe}_{72}\text{B}_{28}$ and $\text{Ni}_{80}\text{B}_{20}$. Copper grids from electron microscopy accessories, pasted with an organic collodion film, had to serve as a carrier for the fragile samples, which were sputtered directly onto the copper grid. After sputtering the collodion film was washed off with acetone. The specimens were proven to be amorphous by transmission electron diffraction. Crystalline samples were produced from amorphous ones by heat treatment in argon atmosphere. Crystallization heat treatment finally lets amorphous $\text{Fe}_{80}\text{B}_{20}$ segregate into crystalline Fe_2B and $\alpha\text{-Fe}$ but it should be noted that the crystallization of amorphous $\text{Fe}_{80}\text{B}_{20}$ is a complex process and under certain conditions even other phases can temporarily be stable /11,12,13,14/.

IV - OVERVIEW ON THE ABSORPTION BEHAVIOUR AT THE BORON K-EDGE

Figure 2 shows the structure of the B-K-absorption coefficient as obtained with elemental boron (upper curve). In the case of alloys fig.2 shows the B-K-absorption coefficient after subtracting the contribution of iron or nickel. The following phenomena can be observed:

- In the case of elemental boron the absorption coefficient decreases

Fig.2. Boron K-absorption in different specimens

to the background value at 260 eV, i.e. within 80 eV, which is much faster than known from the elements commonly studied, but similar to XAS results from other light elements like carbon or nitrogen.

- In the case of the alloys the steep rise of the absorption is followed by a very steep decrease and a second absorption maximum at approximately 200 eV. In the amorphous case the absorption coefficient decreases continuously to the background, whereas in the crystalline case there are slight oscillations till 240 eV. It should be mentioned that cooling the samples to liquid nitrogen temperature does not influence the results in a significant way.

- The intense, sharp peak of half-width 0.7 eV is located at 192.9 eV for the crystalline sample and at 193.2 eV for the amorphous one.

Since the measurements presented in figures 2 and 3 were not taken with maximum energy resolution, the peaks appear a little broader.

- Between 195 and 210 eV the oscillations for amorphous and crystalline samples differ clearly. Peak positions are at 198.5 eV and at 202 eV for the amorphous sample and at 198, 200 and 202.5 eV for the crystalline one. The restriction of the spectra to the narrow energy range between 190 eV and 230 eV makes conventional EXAFS data analysis impossible.

V - THEORETICAL CALCULATIONS, COMPARISON WITH EXPERIMENTAL DATA

Müller et al. /15,16/ have shown, that the K-edge X-ray absorption coefficient can be understood as a product of a matrix element $P(E)$, only weakly dependent on the energy, and the p-projected density of empty states, due to the transition rule for an initial 1s-state:

$$\mu(E) \propto P(E) \cdot \text{DOS}(E) \quad (2)$$

Thus the attempt was made to understand the spectra using the band structure of the alloys.

For the calculation of the DOS of Fe_2B a fully selfconsistent band structure calculation was performed, starting from the unit cell, which was constructed from crystallographic data /17,18/. The calculation is based on the linear muffin-tin formalism (LMTO)/19,20/, using the atomic sphere approximation (ASA) and the local density approximation for the exchange and correlation potentials /21/. Theoretical results for amorphous Fe-B alloys /22/ are based on a numerical calculation by means of continued fraction algorithms /23,24/ using the canonical site- and distance-dependent tight-binding Hamiltonians described in /25/. The calculations start from structural models for amorphous Fe-B alloys, set up by Fujiwara /26,27/ and Zweck /28/. Both of them yield partial pair correlation functions, which are in good agreement with those obtained by neutron diffraction using the method of isotopic substitution /29/. The Fermi level in Fe_2B can be identified using the binding energy for B-1s-electrons in Fe_2B , which was found experimentally to be 188.7 eV

/30/ or 187.6 eV /31/. Binding energies for amorphous TM-B-alloys were not available from literature.

Using figure 3 one can compare experimental and theoretical data.

Fig.3. Boron K-edge
Comparison Experiment-Theory

Essentially three aspects have to be noticed:

- good coincidence in the range from 194 to 215 eV
- non-coincidence for the peak at 193 eV
- energy shift of approximately $\Delta E = 4$ eV between theoretical and experimental scale.

VI - ENERGY RANGE BETWEEN 194 eV and 215 eV

Crystalline Fe_2B :

The calculated DOS curve still does not involve many-particle effects, the most important of which is the filling of the core hole and the decay of the excited state. These effects can be phenomenologically incorporated by convoluting the raw data with a Lorentzian broadening function whose width is equal to the sum of the inverse lifetimes of the core hole and the excited electron /15,16/. The broadened curve is the dashed line in fig.3b. The experimental curve for crystalline Fe_2B reflects quite well the energy positions of the maxima in the DOS curve whereas their intensities fit not so well.

The question why the absorption structure vanishes above 220 eV cannot be answered by this calculation. The answer might be found in the energy-dependence of the matrix element required for the full description of the absorption coefficient, theoretical values for this are, however, not available.

Amorphous $\text{Fe}_{80}\text{B}_{20}$:

The calculated curves for the amorphous alloy don't need to be broadened, since they are less energy-resolved. The conformity of experiment and theoretical calculations is rather obvious for the model of Zweck compared to that of Fujiwara.

VII - PEAK AT 193 eV

It has been reported that the behaviour of soft X-ray absorption edges (in this case K-absorption edges of light elements) is very complicated and far from being completely understood. While up to this point the absorption process was regarded within an one-electron picture, for the edge region a many-body theory was developed (MND-theory), which is able to describe exciton-like energy levels in metals due to possible ineffective screening of charges /32,33/. This picture, which was already successful for explaining the Li-K-edge and the Na-L-edge, might lead to an explanation for the results obtained here. It is

worthwhile to note that similar to the present results also in TiB_2 , a sharp XAS-peak was observed, together with an XES-peak, located at the considerable distance of approximately 10 eV below the absorption edge /34,35/. This points to something similar to a band gap, also visible in fig. 3b.

The multiple scattering approach, on the other hand, commonly using the computer code of Durham et al. /36/, is also able to describe very sharp XANES-peaks /37/. In addition it can be used to predict their shifts to lower energy caused by an increasing nearest neighbour distance /38/. This shift also occurs during the crystallization of amorphous $\text{Fe}_{80}\text{B}_{20}$.

Regarding the band structure, the '192 eV-peak' can not be directly understood. The shape of the s-band in the DOS calculations for amorphous $\text{Fe}_{80}\text{B}_{20}$ is very tempting. Transitions to this band are forbidden, but the states at this energy are not of pure s-symmetry, furthermore, they have p-parts, which must be taken into account.

It should be reminded that neither the matrix element factor from equation 2 was discussed, nor is there a complete understanding of the influence of the core-hole on the spectra /39,40,41/. It can be hoped that with increasing theoretical treatment the different approaches can be merged into an unique picture and that furthermore an explanation for the energy shift between the experimental and the theoretical scale can be given.

VIII - BORON K-EDGE IN OTHER TM-B-ALLOYS

The results for amorphous $\text{Ni}_{80}\text{B}_{20}$ are the same as those for amorphous $\text{Fe}_{80}\text{B}_{20}$. Since the boron states change only by a negligible amount when bound to Ni instead to Fe it can be concluded that the boron surrounding in a- $\text{Ni}_{80}\text{B}_{20}$ is similar to that in a- $\text{Fe}_{80}\text{B}_{20}$, according to results obtained by neutron diffraction /42/.

The results for other compounds have shown the great sensibility of the B-K-edge for distinct structures and phase segregation.

IX - CONCLUSIONS

X-ray absorption measurements of the B-K-edge with different iron- and nickel-boron alloys are presented. The spectra of amorphous $\text{Fe}_{80}\text{B}_{20}$ and crystalline Fe_2B are discussed in detail. For the low energy parts of the spectra analogies to similar physical observations are given. The high energy parts agree well with DOS-calculations which were done by Fembacher et al. for two different structural models of amorphous $\text{Fe}_{80}\text{B}_{20}$.

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