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## X-RAY ABSORPTION STUDIES OF $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$ AMORPHOUS AND NANOCRYSTALLINE ALLOYS

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The nanocrystalline state of the formally amorphous alloy  $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$  is achieved by a heat treatment at temperatures between 500°C and 600°C. The XANES and EXAFS methods were applied for investigation of local structure and chemical bonding around Fe atoms in amorphous and nanocrystalline alloys. The Fe *K* absorption spectra were measured in the transmission mode at room temperature for  $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$  amorphous and nanocrystalline alloys and compared with the spectra for Fe metallic foil and  $\text{Fe}_3\text{Si}$  polycrystalline samples.

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Fe-based nanocrystalline alloys obtained through suitable annealing treatments of particular amorphous ribbons, i.e., Fe-Cu-Nb-Si-B alloy constitutes an interesting new class of metastable metallic systems. Nanocrystalline materials are single-phase or multiphase polycrystals with crystallite sizes in the nanometer range, typically 5–50 nm. They can be produced by processes such as compaction of nm-size powders, deposition techniques or by crystallization from the amorphous state [1]. Nanocrystalline Fe-Cu-Nb-Si-B alloy with excellent soft magnetic properties has become one of the attractive materials. The alloy is obtained from rapidly solidified amorphous ribbons by controlled crystallization at some temperatures. There are mainly two phases in the alloy with the optimum magnetic properties: a bcc Fe-Si solid solution and some residual amorphous phase [2].

X-ray absorption spectroscopy concerns the study of electronic transition from atomic inner shells to unoccupied electron states. X-ray absorption near edge structure (XANES) contains information on chemical bonding of the absorbing ion and local angular geometry of its nearest atomic surroundings, while extended X-ray absorption fine structure (EXAFS) examines the averaged distances from an absorbing atom to nearest atomic shells. The absorption spectroscopy was selected as the primary structural probe for this study because it is sensitive to investigated element and very well suited for study of changes in the local atomic environment, occurring in alloys during heat treatment.

In this work we have investigated the local structure of the nanocrystalline  $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$  alloy which consists of iron-silicon crystallites being only a few nanometers in size and surrounded by a residual amorphous phase. This fine composite structure has been found to yield superior soft magnetic properties. This alloy system is very interesting for physical investigations and important for technical applications because of its very soft magnetic behavior displayed by the nanocrystalline phase.

The amorphous alloy of the nominal composition  $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$  was a commercial ribbon FINEMET produced by Vacuumschmelze GMGH in Hanau. Ribbons of the  $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$  amorphous material were heated at the temperature 500°C for 0.5 hour and 540°C for 1 hour. After heat treatment of the alloys, the X-ray diffraction of Co  $K_\alpha$  radiation demonstrated peaks of  $\alpha$ -Fe(Si) phase while the as-quenched alloy showed a typical amorphous halo. The lattice constant of the nanocrystalline phase was found to be 2.838 Å. From the value of the above lattice constant and lattice constants of  $\alpha$ -Fe (2.8664 Å) and  $\text{Fe}_3\text{Si}$  (5.637 Å), we determined the averaged composition  $\text{Fe}_{80}\text{Si}_{20}$  of the nanocrystalline phase.

The Fe  $K$  edge absorption spectra were measured at the station XAS1 of the synchrotron radiation laboratory LURE in Orsay. A Si channel-cut monochromator and (331) reflection was used. The absorption spectra were recorded at room temperature in the transmission mode. The photon energy scale was calibrated in such a way that the  $K$  absorption edge for Fe metal was placed at the photon energy 7112.5 eV. The XANES spectra were normalized at the photon energy 7175 eV.

The Fe  $K$  edge XANES spectra for the amorphous and nanocrystalline  $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$  alloys are compared with XANES spectra for the  $\alpha$ -Fe foil and the  $\text{Fe}_3\text{Si}$  powdered sample in Fig. 1. The XANES edges of the  $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}\text{B}_7$  alloys are almost structureless except the shoulder at the pre-edge. It is important to stress that the XANES spectrum of  $\alpha$ -Fe foil wiggles up and down with respect to the XANES spectrum for the amorphous alloy. We interpret this behaviour that the chemical state of the Fe atoms in the amorphous alloy and after heat treatment at 500°C remains unchanged and is similar to the Fe metal.

It is not the case for the alloy after another heat treatment at the higher temperature 540°C. The XANES spectrum of this alloy exhibits additional increase in absorption in the energy range from 7113 to 7125 eV towards the XANES spectrum for  $\text{Fe}_3\text{Si}$ . In the frame of the one-electron model of X-ray absorption it can be interpreted as increase in density of unoccupied  $p$ -type electron states around Fe atoms. We suppose that it results from bonding of the Si atoms to the Fe atoms only during annealing at higher temperature. It seems that the Fe  $K$  edge XANES spectrum is very sensitive to the presence of Si atoms in the neighbourhood of Fe atoms.

The EXAFS data analysis was performed by using the program "EXAFS" made by Bonnin et al. [3]. A linear function was fitted to the pre-absorption edge region and subtracted from the spectrum. The extended fine structures were then

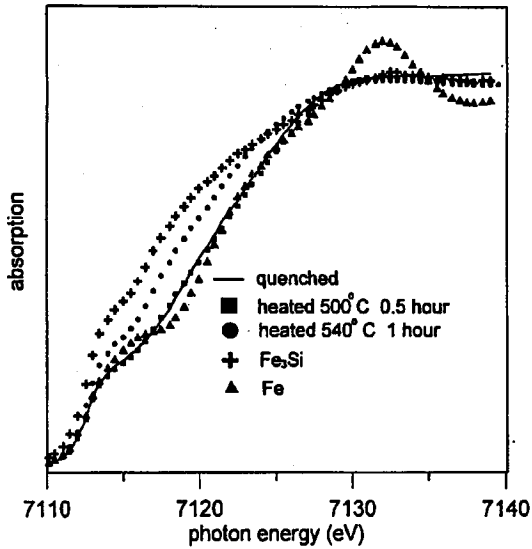


Fig. 1. XANES spectra at Fe *K* edge: 1 — the amorphous alloy (solid line), 2 — the alloy after heat treatment at 500°C through 0.5 hour (squares), 3 — the alloy after heat treatment at 540°C through 1 hour (circles), 4 — Fe<sub>3</sub>Si (crosses), 5 — α-Fe (triangles).

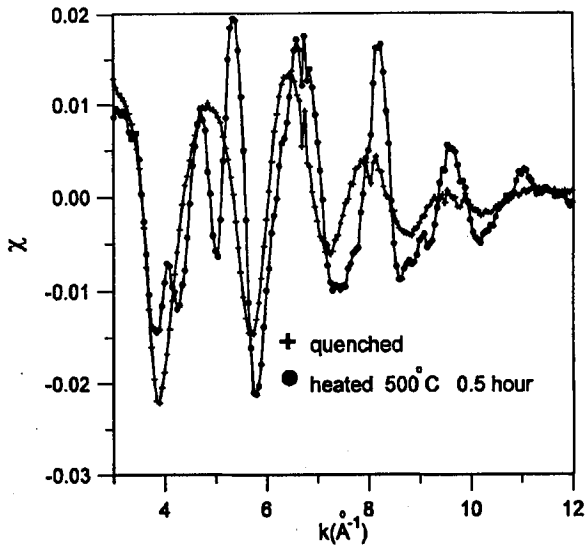


Fig. 2. Fe *K* EXAFS oscillations for the Fe<sub>73.5</sub>Cu<sub>1</sub>Nb<sub>3</sub>Si<sub>15.5</sub>B<sub>7</sub> amorphous alloy (crosses and line) and after heat treatment at 500°C through 0.5 hour (circles and line).

isolated and normalized to the edge step height and energy. The oscillatory parts of the absorption coefficient are shown in Fig. 2.

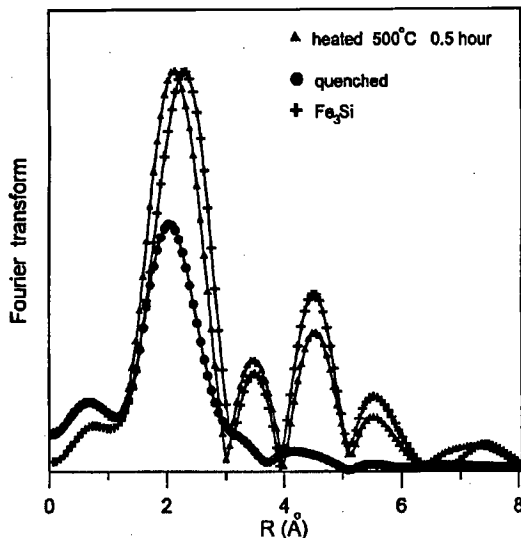


Fig. 3. Fourier transform of Fe *K* EXAFS for alloys studied and Fe<sub>3</sub>Si.

The Fourier transforms (FT) were calculated in the  $k$  range from 3 to 10 Å<sup>-1</sup>, applying a Hamming window and weighting factor  $k^3$ . The FT magnitudes are presented in Fig. 3. The Fourier transform of  $k^3\chi(k)$  for as-quenched alloy shows only one peak and is characteristic of an amorphous structure. The FT for the Fe<sub>73.5</sub>Cu<sub>1</sub>Nb<sub>3</sub>Si<sub>15.5</sub>B<sub>7</sub> alloy, heated at 500°C during 0.5 hour, is slightly different in magnitudes and peak positions from the FT for Fe<sub>3</sub>Si. It can be caused by different distribution of silicon atoms around the central Fe atom in both samples, and a big number of structural defects in the case of nanocrystalline grains due to boundary effects and a presence of other elements.

In summary, the Fe *K* edge XANES of a nanocrystalline Fe<sub>73.5</sub>Cu<sub>1</sub>Nb<sub>3</sub>Si<sub>15.5</sub>B<sub>7</sub> alloy is influenced by the presence of the Si atoms bonded to the Fe atoms, while the Fe *K* edge EXAFS spectra are sensitive to the local atomic ordering around Fe atoms. The XANES and EXAFS investigations, if performed together, promise to get a new insight into nature of nanocrystallization of alloys.

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