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A NEW METHOD FOR THE DETERMINATION OF THE TOTAL STRUCTURE FACTOR
OF AMORPHOUS MATERIALS BY ENERGY-DISPERSIVE X-RAY DIFFRACTION
(VARIABLE λ -METHOD)

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Résumé - Une nouvelle méthode est proposée pour déterminer le facteur de structure total de matériaux amorphes à l'aide d'une technique d'analyse en énergie des rayons X diffractés (EDXD, méthode de la longueur d'onde variable). Cette méthode est fondée sur l'évaluation directe du spectre d'énergie du faisceau primaire à partir des données de diffraction sans appliquer aucun procédé itératif. Les facteurs de structure de plusieurs alliages amorphes (Be Ti Zr, Ni Zr et Ni Co Zr) obtenus de cette manière sont comparés à ceux fournis par la méthode classique de dispersion angulaire (ADX, méthode du 2θ variable).

Abstract - A new method was developed for the determination of the total structure factor of amorphous materials using the energy-dispersive X-ray diffraction technique (EDXD, variable λ -method). It is based on the direct evaluation of the energy spectrum of the primary beam from the diffraction data without applying iterative procedures. The total structure factor for several amorphous alloys (BeTiZr, NiZr and NiCoZr) derived in this way is compared to the one obtained from the angular dispersive X-ray diffraction technique (ADX, variable 2θ -method).

I - INTRODUCTION

The static structure factor $I(q)$ contains important information on the topological and chemical correlations in a many particle system. This fact is especially true for alloys where the partial structure factors have to be considered. The latter may be determined by several methods [1], however, precise measurements of the diffracted intensities are necessary in order to obtain meaningful results.

$I(q)$ can be evaluated by X-ray diffraction as a function of the length of the diffraction vector $q = 4\pi \sin\theta/\lambda$. This can be accomplished by varying the scattering angle 2θ using monoenergetic radiation (λ : wavelength of the X-rays). Such a method is called angular dispersive X-ray diffraction (ADX) or variable 2θ -method. Here θ defines the Bragg- and 2θ the scattering-angle. Since the development of Ge- and Si-X-ray detectors with high energy resolution (≈ 400 eV), a variation of the wave vector q is also possible by measuring the intensity as a function of the energy E at several fixed angles 2θ . This procedure constitutes the energy dispersive X-Ray diffraction (EDXD) or the variable λ -method, as the wave length λ is varied in order to change q .

In both methods, the diffracted intensities have to be corrected for absorption, polarisation, multiple and Compton-scattering. In addition, the data must be normalized with respect to the scattering power per atom. These corrections are straightforward, however, in order to perform them properly, the energy spectrum of the primary beam $I_0(E)$ must be known.

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II - THEORETICAL CONSIDERATIONS

In a first approximation the diffracted intensity $I(E, \theta)$ may be described by /2/:

$$I(E, \theta) = C \{ \epsilon(E) I_0(E) \cdot P(E, \theta) \cdot A(E, \theta) \cdot [I_a(q) + I_{ms}^{coh}(E, \theta)] + \epsilon(E) \cdot I_0(E') \cdot P(E, E', \theta) \cdot A(E, E', \theta) [I_c(q') + I_{ms}^{incoh}(E, E', \theta)] \}, \quad (1)$$

$$\text{where } (1) \quad q = [2/(\hbar c)] \cdot E \cdot \sin \theta, \quad (2)$$

$$q' = q \left[1 - \left(\frac{2E}{m_0 c^2} \right) \sin^2 \theta + \left(\frac{E}{m_0 c^2} \right) \sin^2 \theta \right]^{1/2} \cdot \left[1 - \left(\frac{2E}{m_0 c^2} \right) \sin^2 \theta \right]^{-1} \quad (3)$$

$$\text{and} \quad E' = E \cdot \left[1 - \left(\frac{2E}{m_0 c^2} \right) \sin^2 \theta \right]^{-1}. \quad (4)$$

$\epsilon(E)$ is the detector efficiency, $I_{ms}^{coh}(E, \theta)$ as well as $I_{ms}^{incoh}(E, E', \theta)$ are the multiple scattering contributions, $I_c(q')$ describes the Compton-intensity and $I_a(q) = \langle f^2 \rangle \cdot I(q) + \langle f^2 \rangle$ contains the formfactors $\langle f^2 \rangle$ as well as $\langle f^2 \rangle$ and the structure factor $I(q)$. The prime at q' and E' indicates quantities shifted from q and E by the Compton-effect. The expressions for A and P have been discussed in detail elsewhere /2,3/.

We recognize, that $\epsilon(E) \cdot I_0(E)$ should be known in equ. (1) in order to interpret the data correctly. The task can be accomplished as follows:

Introducing the variables q and E instead of θ and E and in the limits of $E \geq 20$ keV as well as $q \leq 5 \text{ \AA}^{-1}$, we get (2)/2/:

$$C \cdot \epsilon(E) \cdot I_0(E) = I_{corr}(E, q) \cdot (I_a(q) + I_c(q))^{-1}. \quad (5)$$

In this expression, the multiple scattering contributions have been omitted for clarity. They may be incorporated if necessary. The quantity $I_{corr}(E, q)$ can be derived directly from the measurement by analyzing EDXD-data:

$$I_{corr}(E, q) = I(E, q) \cdot \frac{[1 - 0.9735(q/E)^2]^{1/2}}{[1 - 1.947(q/E)^2] \cdot \exp \left\{ \frac{-\mu(E) \cdot t}{[1 - 0.9735(q/E)^2]^{1/2}} \right\}} \quad (6)$$

Thus, equ. (5) gives $\epsilon(E) \cdot I_0(E)$, apart from a constant -, if considered at $q = q_0 = \text{const.}$ and in the limit $q < 5 \text{ \AA}^{-1}$. The analysis can be performed for several q_0 -values, providing $\epsilon(E) \cdot I_0(E)$ -curves scaled with respect to one another by a multiplicative constant. This constant is the ratio of two expressions defined by the curly brackets in equ. (5). Fig. 1 shows a schematic plot of the situation. The analysis of the ADXD-data ($E = \text{const.}$) can now be done in the usual way, however, with an improved Compton correction. From equ. (1), we derive:

$$I(\theta) = C \cdot \{ P(\theta) \cdot A(\theta) \cdot I_a(q(\theta)) + \alpha(E'(\theta)) \cdot P(E'(\theta), \theta) \cdot A(E'(\theta), \theta) \cdot I_c(q'(\theta)) \} \quad (7)$$

$$\text{with} \quad \alpha(E'(\theta)) = I_0(E'(\theta)) / I_0(E).$$

With respect to the analysis of the EDXD-data ($2\theta = \text{const.}$), we have:

$$I(E) = C \{ \epsilon(E) \cdot I_0(E) \cdot P(E) \cdot A(E) \cdot I_a(q(E)) + \epsilon(E) \cdot I_0(E') \cdot P(E, E'(E)) \cdot A(E, E'(E)) \cdot I_c(q'(E)) \}. \quad (8)$$

(1) Here, m_0 denotes the electron rest mass, $\hbar = h/(2\pi)$ with h the Planck constant and c the velocity of light.

(2) In the remainder of this paper, we use the units E/keV and $q/\text{\AA}^{-1}$, then $2/(\hbar c) = 1.0135$ (see equ. (2)).

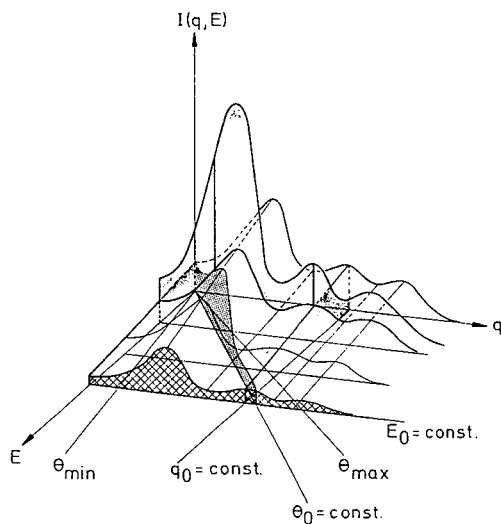


Fig. 1 - Schematic plot of the diffracted intensity surface $I(E, q)$ in the q - E -plane. Several cuts through this surface as performed by the ADXD (E_0) and EDXD(θ_0)-methods are indicated. The cut $q_0 = \text{const.}$ shows the energy spectrum of the primary beam as long as $q_0 < 5 \text{ \AA}^{-1}$. θ_{max} and θ_{min} refer to the available angular range ($\theta_{\text{max}} = 90^\circ$).

In this case, the data taken at fixed 2θ cover only a limited q -range (see Fig. 1), so that the results from several angular positions have to be scaled with respect to one another. This can only be achieved with a proper knowledge of $\epsilon(E) \cdot I_0(E)$. The quantity $\epsilon(E)$ should be known from the detector specification.

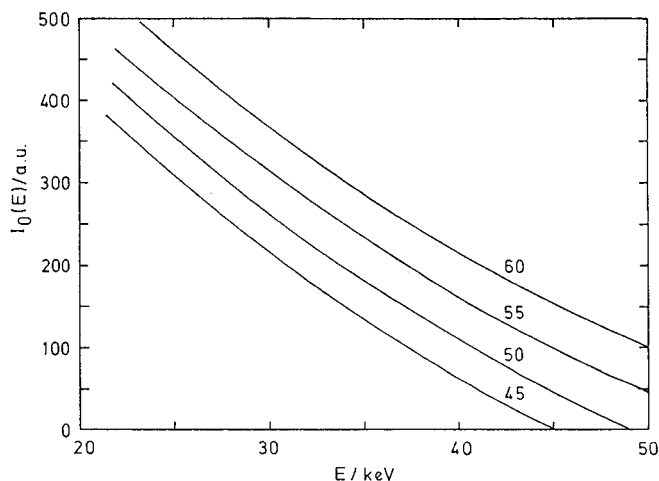


Fig. 2 - The primary beam intensity $I_0(E)$. the parameters are the tube voltages U in kV. The tube current was set around 14mA.

III - RESULTS

With the help of a conventional X-ray equipment, data have been taken for several amorphous alloys using ADXD (2 θ -method) and EDXD (λ -method). The detector was a Ge-crystal with an energy resolution of about 400 eV and an efficiency of $\epsilon(E) \approx 1$ over the range of energies interesting here. Transmission geometry under nonfocussing conditions was applied throughout. The energy spectrum of the primary beam $I_0(E)$ for several values of the tube voltage was derived from EDXD-data of Be_{37.5}Ti_{62.5} (45, 55, 60 kV) and of Fe₇₈B₁₃Si₉ (50 kV) as described above. The results are shown in Fig. 2.

Data were also taken for the amorphous alloys Be_{37.5}Ti_{62.5}, Be₄₀Ti₅₀Zr₁₀, Ni₃₅Zr₆₅ as well as Ni₁₈Co₁₇Zr₆₅ both in the ADXD- and EDXD-modes. Some of them are reproduced in Figs. 3 to 5.

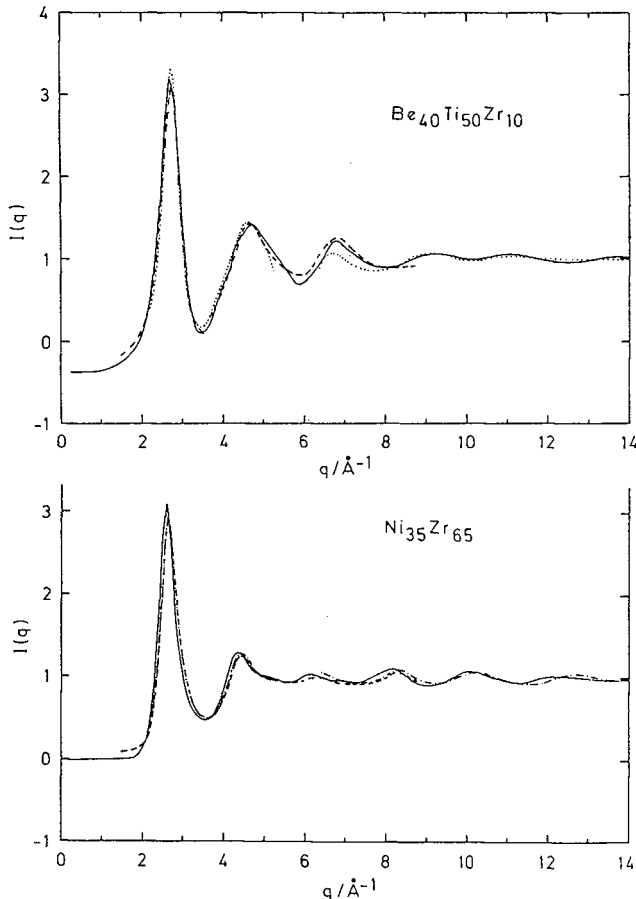


Fig. 3 - $I(q)$ -data for Be₄₀Ti₅₀Zr₁₀ as determined by the 2 θ -method (ADXD) and the λ -method (EDXD). The overlap of the different EDXD-data sets, taken at various fixed 2 θ -positions (6°, 10°, 20°, 30°) is clearly seen.

Fig. 4 - The same as Fig. 3 for Ni₃₅Zr₆₅.

IV - CONCLUSIONS

- i) Inspection of Fig. 2 indicates that the spectrum of the primary beam $I_0(E)$ decreases continuously towards higher energies. The total integrated intensity of the Bremsstrahlungs-spectrum is proportional to the square of the tube voltage, as was predicted /4/.
- ii) The agreement between the $I(q)$ -functions derived from ADXD- and from EDXD-data is convincing. Certain deviations (peak heights, small q -range of a few of the EDXD-runs) have still to be examined.

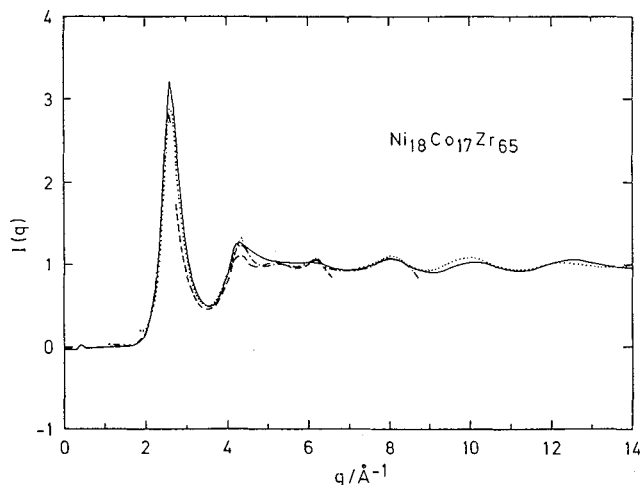


Fig. 5 - The same as Fig. 3
for $\text{Ni}_{18}\text{Co}_{17}\text{Zr}_{65}$

- iii) Since $\text{Be}(Z=4)$ doesn't show up in the alloy $\text{Be}_{37.5}\text{Ti}_{62.5}$ in X-ray diffraction, the Ti-Ti-correlations dominate the measured $I(q)$. These correlations stretch out far in q -space, pointing towards a well defined next neighbour shell (tendency to form Ti-clusters) /5/. The same is true for the $\text{Be}_{40}\text{Ti}_{50}\text{Zr}_{10}$ -alloy. However, the oscillations show a different period indicating a different distance of the first shell (effect of substitution of Ti by Zr). In the cases of $\text{Ni}_{35}\text{Zr}_{65}$ and $\text{Ni}_{18}\text{Co}_{17}\text{Zr}_{65}$, the scattering powers of Zr ($Z=40$) on one hand and of Co($Z=27$) as well as Ni($Z=28$) on the other hand are not so different, hence both components are seen in $I(q)$. The substitution of Ni by Co doesn't change the overall structure, since the general appearance of $I(q)$ remains the same. Therefore, one may be able to separate $I_{\text{ZrZr}}(q)$ from $I_{\text{NiNi}}(q)$ by analysing precise data for both the alloys
- iv) Covering the full range available in the E - q -plane with the help of the EDXD-method for many fixed 2θ -positions will give the possibilities to derive a large number of $I(q)$ -functions, each of them determined at a different value $E=\text{const.}$ In fact, if the detector resolution is 400 eV and if the energy range amounts from 20 to 50 keV, we may obtain as many as seventy-five identical $I(q)$ -curves. This multitude may help to clarify the corrections and to derive precise $I(q)$ -data. Finally, it should be mentioned that, if an absorption edge is present within the energy range available, one may hope to get valuable informations on anomalous diffraction and eventually on partial structure factors.

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