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ANOMALOUS SCATTERING METHOD

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НОВОСИБИРСК

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Abstract

In this work wiggler of VEPP-3 is used for generation two beams of synchrotron radiation. After focusing monochromator, both of them have energy near Ni K-edge, but with 20 eV difference one from other. At the sample position two beams separated at 2.3 mm. Simultaneously registration of two X-ray diffraction patterns at different energy was made by two position sensitive detectors OD-2. The comparison of two diffraction patterns, registrated at different energy, clear show the anomalous scattering effect for the test sample NiO. This method was used for the investigation the behaves of the Ni atom during the solid state chemical reaction $NiO+MoO_3 \rightarrow NiMoO_4$ at T=600–800 C°. This method gives the anomalous scattering signal when the Ni atoms appear in the structure of molybdenum oxide phase. The kinetics of formation of β— $NiMoO_4$ was obtained. At different temperatures Ni atoms occupied different positions in the structure of β—$NiMoO_4$: at 650 C° — the sites of crystal lattice, at 690 C° — the interstitial positions.

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1.Introduction

The anomalous scattering effect is used in X-ray structural analysis for determine the crystallographic position of atoms having similar Z values. The anomalous scattering method is used most efficiently on synchrotron radiation (SR) sources, since in this case it is possible to closely approach the K-edge (or L-edge) of absorption, which leads to the most increasing of the anomalous effect.

In the conventional anomalous scattering method used energy, near the K-edge of absorption for the first X-ray diffraction patterns. After that, the monochromator rotates and reach the used energy, ~100 eV less the K-edge, for the second X-ray diffraction patterns.

The fact that the atomic scattering factor have different values for different energy leads to changes in the intensities of the reflections of X-ray patterns.

The analysis of two X-ray diffraction patterns, recorded using different energy, enable the position of the atoms having similar Z values to be determined.

However, if the crystallographic position of atoms is to be determined during high-speed structural transformation, the traditional anomalous scattering method becomes unsuitable since a comparison of X-ray patterns obtained at different energies, and hence at different times is made impossible. Therefore, for the solution of such problems, it is necessary that two X-ray patterns should be recorded simultaneously using two energies.

2. Phase-space analysis of the synchrotron radiation from wiggler VEPP-3

In the tree-poles wiggler VEPP-3 the trajectory of electrons is three connected arcs of 3 circles, the radii of which are determined by the magnetic field of the poles (+19.9 kGs, −19.8 kGs, +19.9 kGs correspondingly). Consequently, the generation of synchrotron radiation will occur in the directions coinciding with the direction of the tangents to these arcs. Tangents which will be parallel to each other can be draw to any two neighboring arcs. Thus, the SR will go by two beams in the direction of that tangents and parallel one to the other. Consequently, the electrons occurring on different arcs and hence spaced from each other will generate SR in one and the same direction (Fig. 1,*a*). Therefore, two point of sources of synchrotron radiation are visible simultaneously in direction coincide with axes z.

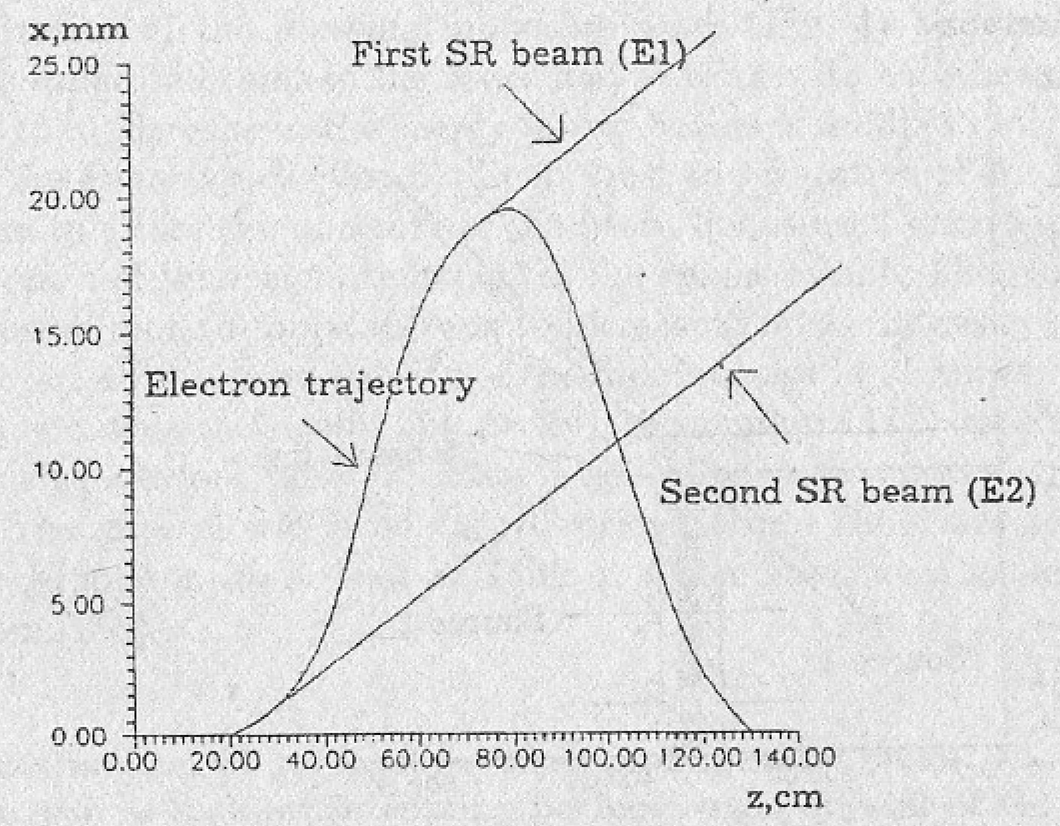
The generation of the SR in the wiggler is more conveniently analyze using the phase-space technique. With a knowledge of the trajectory of the electron beam in the horizontal $x(z)$ plane (Fig. 1,*a*), the phase-space diagram $x'(z)$ displayed in (Fig. 1,*b*) can be easily constructed. The directions of radiation to different beam lines are shown by lines within the ellipse. The diagram shows, that 5-th beam line is installed at the angle of 14 mrad to the axes of the wiggler, and that SR generates in the same direction from two points of trajectory. The coordinates of these points correspond to coordinates of the points of intersection of lines with ellipse. As Fig. 1,*b* show, such intersections are two. The distance between the two points of intersections equals to the visible spacing between the SR sources. In particular, in the direction of the 5-th beam line the sources are visible at distance of 1.14 cm.

The phase diagram for electron beam coincides with the phase diagram of SR at $z = 0$, but it transforms when z increase. At a distance of $z = 17$ m from the wiggler SR phase diagram transforms and takes the form, a part of which is shown at Fig. 2. It is seen, that SR beams are partially overlapped (shaded region in Fig. 2).

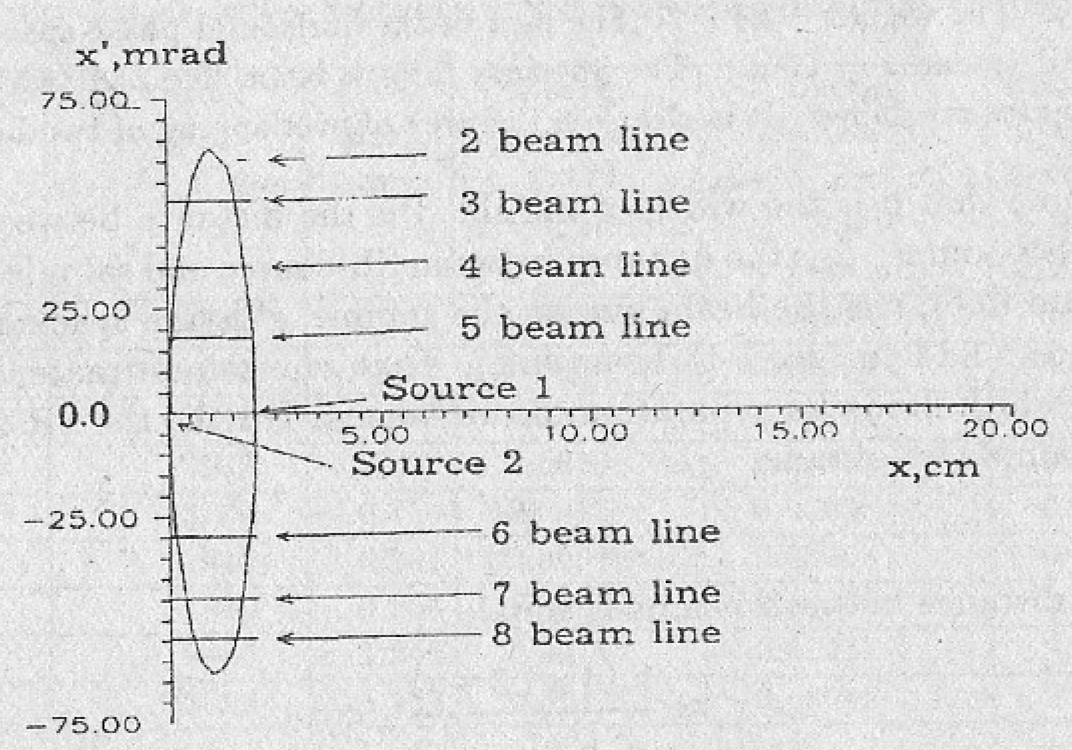
Naturally, the radiation from two sources incident on a monochromator at different angles, therefore, after monochromator two diffracted beams will have different energy E_1 and E_2.

In order to prevent the overlapping of two monochromatic beams a slit should be installed in front of the monochromator (Fig. 3).

However, as the beams are separated in such a manner, a portion of radiation "cut" by the slit will be lost, of the beams causes the loss of a part of intensity, which will lead to decrease of the radiation density on the sample.



a



b

Fig. 1. The wiggler VEPP-3. *a* — The electron trajectory in the wiggler. Two SR beams generation at different points of electron trajectory is shown. *b* — The horizontal phase-space discription of the electron beam and SR at the source position (plane $z = 0$). The directions of the different beam lines are shown. The coordinates of two sources viewed in 5-th beam line are shown.

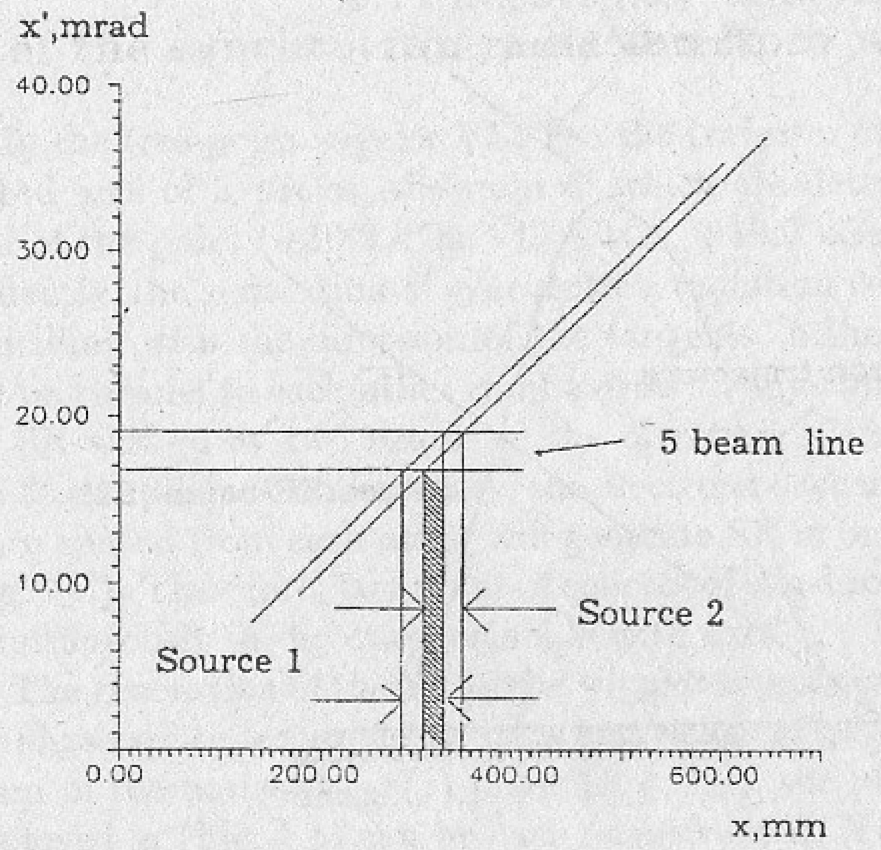


Fig. 2. The wiggler VEPP-3. The part of the horizontal phase-space distribution of SR (plane $z = 17$ m). The aperture of 5-th beam line and two SR beams x-coordinates are shown. It is clear see the area of overlapping of two beams.

Assume that h is the width of the slit, l is the distance between the slit and the SR-source, L-is the distance between SR-source and sample (20 m for 5-th beam line), r is the beam size on the sample, r' is the spacing between SR sources (1.14 cm. for 5-th beam line). Than one can estimate the size of the slit, which needs for separation of two beams. For the the SR beam size on the sample we obtain:

$$r \approx \frac{h \times L}{l}$$

and the distance between beams is equal:

$$r' \approx \frac{1.14 \times (L - l)}{l} \quad \text{cm}$$

The condition of the separation of beams is: $r' > r$. On the other hand, the spacing between the beams and the size of the beam are limited by the aperture of the beam line channel $r < 2$ cm. and $r' < 2$ cm. Than we can find $h \sim 0.72$ cm, $l \sim 7.3$ m. In this case, the size of the beam will be 2 cm and the distance between the beams will be 2 cm, i.e. the beams will touch one another by the edges.

The utilization of the focusing monochromator (Fig. 4) also gives the possibility to separate beams in the space and to work with each beam individually. As the difference in the energy of two beams is small (18 eV), than both beams are focused well (Fig. 5). In contrast to separation of the beams by the slit, in this case the aperture of the beam line is used completely for each of sources, and there is no "cutting" of the beams by slit. Therefore the using of focusing monochromator leads to increasing in the intensity on the sample in about 4 times, and density of the flux increase in 20 times.

The triangle asymmetrically cut perfect germanium (111) crystal was used as focusing monochromator. That angle of asymmetry was equal to 7 degrees. This crystal was bend in cylindrical form. The characteristics of the monochromator are present at Table 1. Calculation were made using formulas from [1, 2].

Table 1.

Estimation of parameters of monochromatic beam. Monochromator is assimetric cutting perfect single crystal of Ge (111) reflection is used. Cutting angle is equal 7.00 degrees. Estimation is carrid out for distance betveen crystal-specimen equal 4550 mm

Wavelenth Å	Focusing length, $p = P/Å$, mm	Focal size, mm	Energy resolution, $\Delta\lambda/\lambda$ $p = 4550$ mm	Energy resolution, $\Delta\lambda/\lambda$, $p = P/Å$ (Gunie condition)	Relative distance between beams, $\Delta E/E$
1.000	867	0.241	0.0061	0.00076	0.0027
1.100	1694	0.387	0.0046	0.00069	0.0025
1.200	2446	0.518	0.0034	0.00064	0.0023
1.300	3133	0.639	0.0024	0.00060	0.0021
1.400	3764	0.753	0.0015	0.00056	0.0019
1.500	4346	0.862	0.00075	0.00053	0.0018
1.600	4885	0.964	0.00087	0.00050	0.0017
1.700	5386	1.061	0.0014	0.00047	0.0016
1.800	5852	1.154	0.0018	0.00045	0.0015

For changing the wavelength, the crystal — monochromator was rotated around vertical axes.

The sample was installed on the $\Theta - 2\Theta$ goniometer. The diffracted radiation was registrated by two position sensitive detectors OD-2 [3] — one detector for energy E_1, the other for E_2. For overcoming the overlapping of two diffraction patterns at two energies, the lead enclosure was used (Fig. 4).

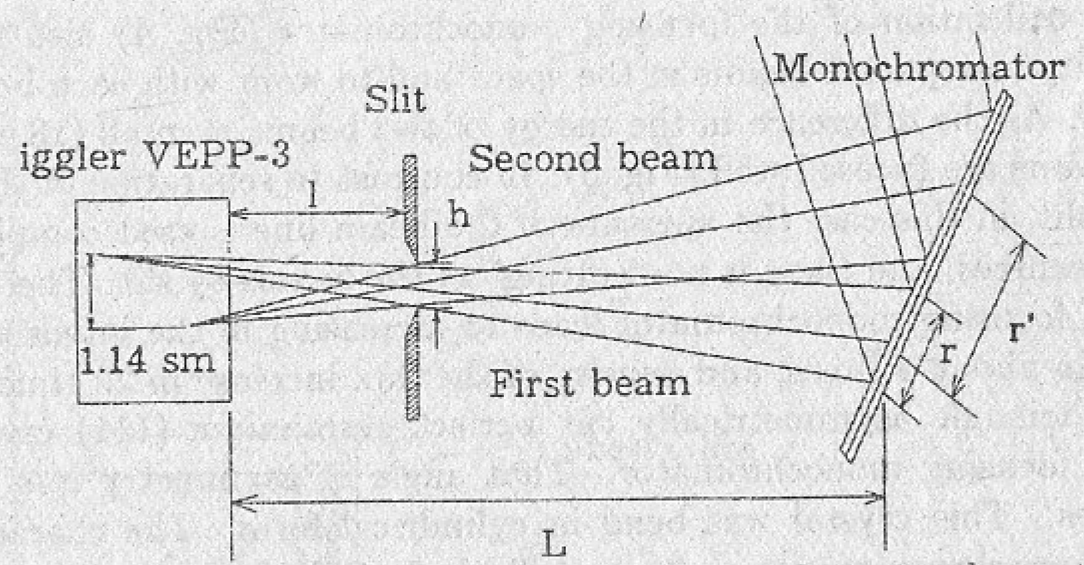


Fig. 3. The scheme of the experiment with slit and flat monochromator. The wiggler is represented by two sources of SR, viewed at distance 1.14 cm. A beam of SR on passing through a slit is separated into two beams.

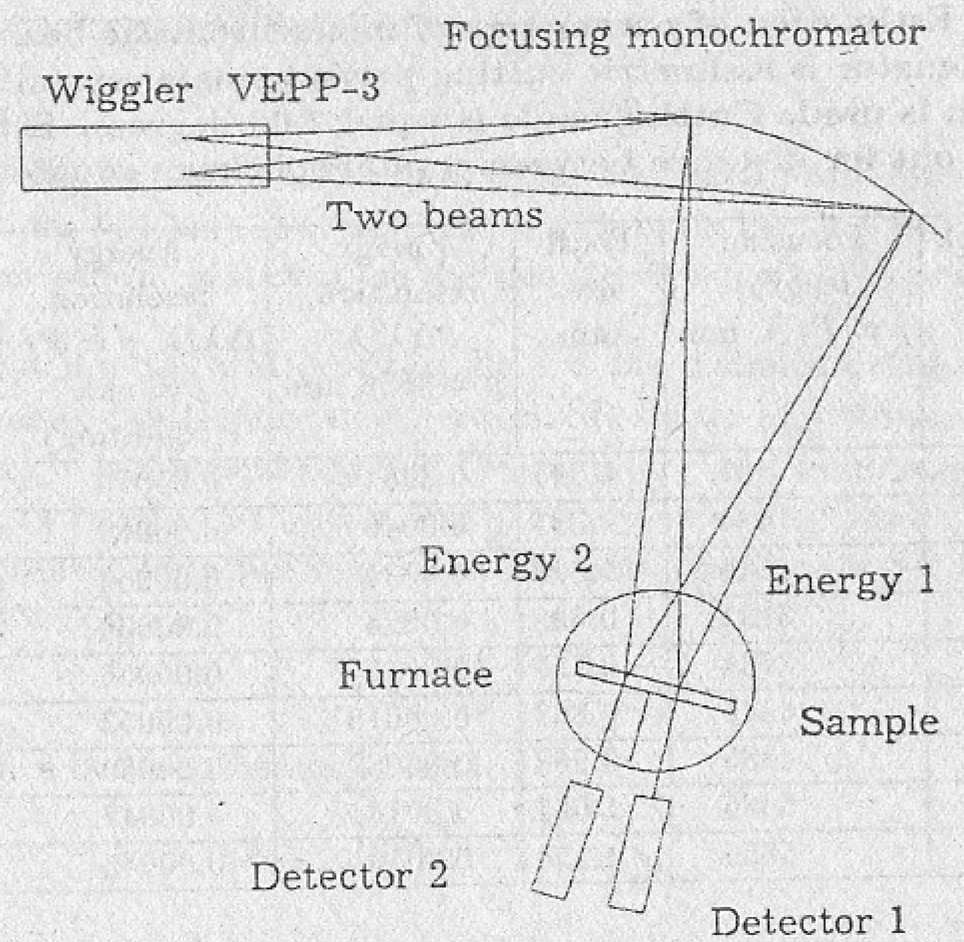


Fig. 4. The scheme of the experiment with two beams using focusing monochromator. A beam of SR on reflecting at bending monochromator is separated into two beams with different energy E_1 and E_2. The both beams are focusing on the detectors. Scattering photons with energy E_1 are detected by detector-1, and with E_2 — by detector-2. Enclosure is used for separation of scattering photons with E_1 and E_2.

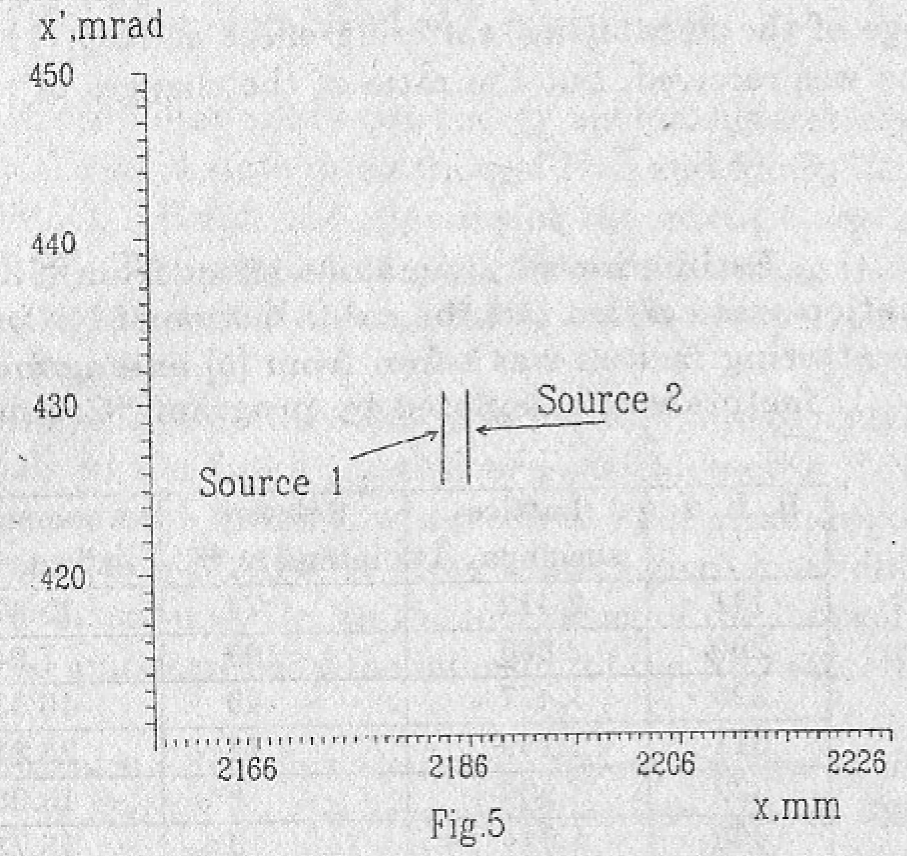


Fig. 5. Two SR beams of the 5-th beam line after the focusing monochromator near the sample.

If the change of the structure is slow, and take place during several hours we use only one detector and selective beam shutter. In this mode of the work only one beam with energy E_1 is using for one frame, the other beam, with energy E_2, was closed by shutter. For the next frame the first beam (energy E_1) was closed and used the second beam (energy E_2), and so on.

3. Test experiment

The mixture of two powder of NiO and MoO_3 was used as the test sample for the method of simultaneously two energy anomalous scattering. For this sample used energies $E_1 = 8300$ eV and $E_2 = 8320$ eV, which lies near Ni K-edge. The registrated anomalous effect for NiO (111) reflection was 18%, and naturally there was no changes of intensities of MoO_3 reflections (Fig. 6). The computer simulation of the NiO diffraction patterns was made with using the atomic structure of NiO [5] for the same energies, but for ideal perfect monochromator (Table 2). The value of anomalous scattering effect in the computer simulation was 15.5% at NiO (111) reflection, and 7.6% at NiO (200) reflection. The ratio of changes in the intensities at NiO (111) and NiO (200) equal 2. When the changes of the both absolute energies was made, for example, more close to K-edge, but with the same difference of energies, the change of the anomalous scattering effect at NiO (111) and NiO (200) reflections was received, but the ratio of the changes of the intensities was the same.

Table 2

Estimation of anomalous effect from NiO.
Estimation was carried out for cubic lattice of NiO. The values of atomic scattering factors was taken from [5] and anomalous dispersion factors was calculated by program "Cromer".

H, K, L	Lattice spacings, Å	Relative intensity, %	Anomalous effect, %
111	2.412	74	15.47
200	2.088	100	7.64
220	1.477	40	10.33
311	1.259	14	23.81
222	1.206	8	13.05
400	1.044	3	15.73
331	0.958	4	34.38
420	0.934	7	18.59
422	0.853	5	21.75

The different anomalous scattering effect at (111) and (200) reflections of NiO is explained by the influence of the interference of waves scattered by different sublatticies. The NiO has trigonnaly distorted FCC lattice. Since the distortions are very small, we can ignore them and write the structure factor:

$$S = 4 \times (f_{ni} \pm f_0)$$

where the sign (−) is used if hkl are odd, and the sign (+) when hkl — even. Than, if hkl are odd, the value of relative change of intensities is equal $dI = 2 * df$ Ni/S and will be bigger in comparison with the relative change of intensities for even hkl.

The interference of nickel and oxide sub lattices is more important than the angle dependence of atomic scattering factor, after that the anomalous scattering effect at NiO (111) is more strong than at NiO (200) in spite of the fact, that the NiO (200) diffracted at more high angle.

4. The "in situ" study the behavior of Ni during $NiMoO_4$ synthesis

The method of the simultaneously two energy anomalous scattering have been used for study the solid state interaction of NiO and MoO_3, leading to the synthesis of $NiMoO_4$. Before the experiment the mixture was homogenized in the AGO-2 [4]. The reaction of synthesis occurs during the heating of a mixture of the powders of NiO and MoO_3 at the temperature about 700 C° degrees and higher.

During the heating, the Ni atoms diffused to the structure of molybdenum oxide phase. It leads to the fast formation of nonstehiometric β-$NiMoO_4$. The kinetic of formation of β-$NiMoO_4$ was received. The structure of the β-$NiMoO_4$ is isostructure to α-$MnMoO_4$. More heating gives more diffusioned Ni atoms in the molybdenum oxiDe, an the increasing of the intensity of the β-$NiMoO_4$ reflections and decreasing the intensity of the NiO reflections was measured.

At different temperature Ni atoms occupied different position in the structure of β-$NiMoO_4$: at 650 C° — the crystal lattice position, at 690 C° — in the interstitial positions. These conclusion was made after analysis of the diffraction patterns, received "in situ" at 650 C° and 690 C° at different energies (Fig. 7, Fig. 8). At 650 C° the anomalous scattering effect take a place at all reflections of β-$NiMoO_4$. At 690 C° the anomalous scattering effect at reflections of β-$NiMoO_4$ is small, but diffusion scattering is mach bigger and is very sensitive to the change of the energy.

During the heating the value of anomalous scattering effect on the NiO reflection was always measured, and used as the beam monitor.

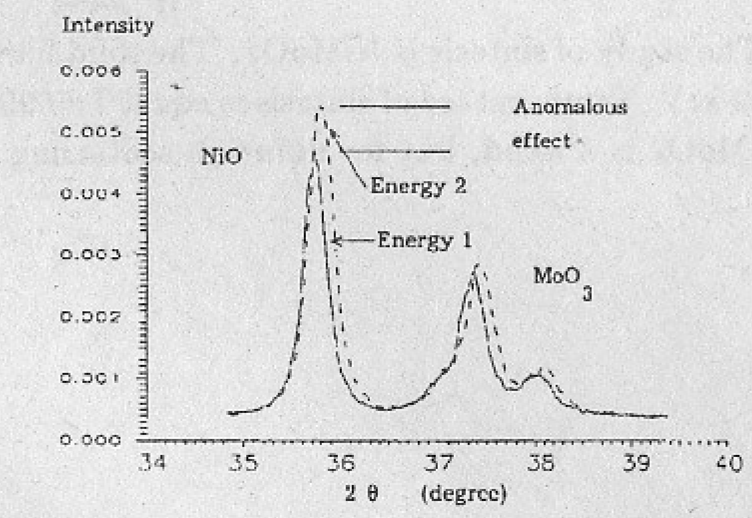


Fig. 6. The test experiment. The sample: mixture of NiO with MoO_3. The diffraction patterns for two energes E_1 and E_2 near Ni K-edge. Anomalous effect is shown.

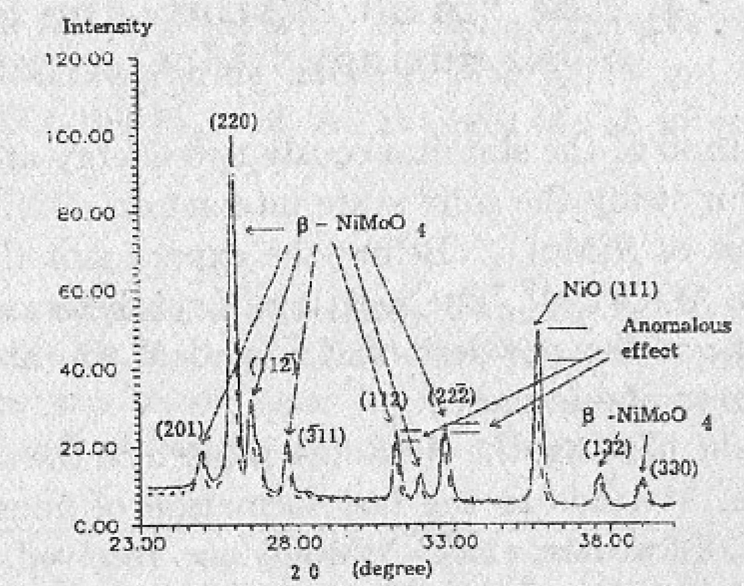


Fig. 7. The study of sintesis is equal T=650 C°. Anomalous effect for NiO and betta-$NiMoO_4$ is shown.

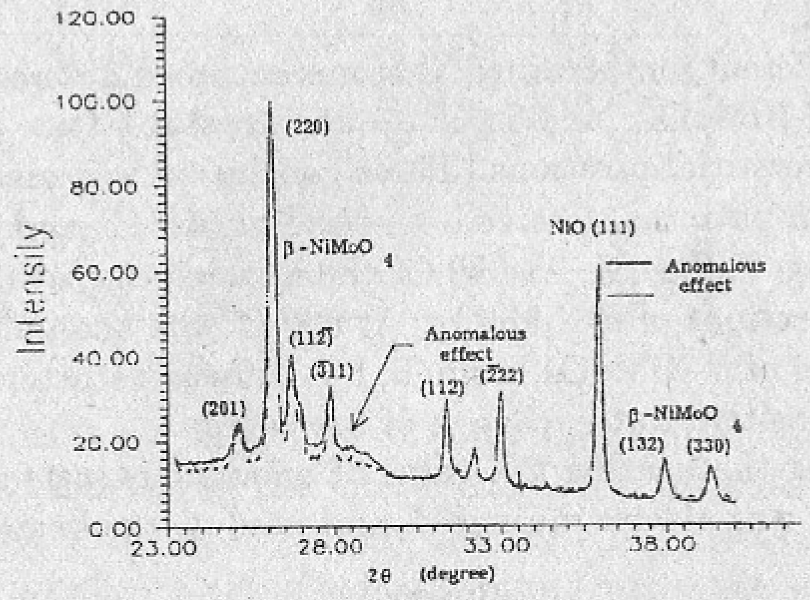


Fig. 8. The study of sintesis is $NiMoO_4$. The solid line $E = 8.30$ keV, the dashed line $E = 8.32$ keV. Temperature of sintesis is equal T=690 C°. The anomalous effect for betta-$NiMoO_4$ is absend, but for diffusion scattering is very big.

5. Acknowledgment

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References

[1] A.N. Popov, A.A. Antson, V.V. Belyaev. Nucl. Instr. and Meth., 282 (1989) 510.

[2] J.R. Helliwell, T.G. Greenhough, etc. Preprint Daresbure Laboratory DL/SCI/P312E (1981), p.30.

[3] V.V. Boldyrev, N.Z. Lyakhov, etc. "The diffractometry with using sinchrotron radiation" (Nauka, Novosibirsk, 1989), p.144.

[4] V.V. Boldyrev. "Technics and methods for activation of nonorganic materials" (Nauka, Novosibirsk, 1991), p.123.

[5] L.I. Mirkin. Reference book for x-ray analisis of powders, (State publ. of phis. and math. lit., Moscow, 1961, p.863.).

[6] S.C. Abrachams and J.M. Reddy. The Journal of Chemical Physics, 43, 7, (1965) 2533–2543.

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