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THE RHOMBOHEDRAL STRUCTURE CONTRIBUTION IN NATURAL GRAPHITES DETERMINED BY NEUTRON DIFFRACTION TECHNIQUE

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Abstract: The neutron diffraction technique was used to determine the contribution of the rhombohedral modification within the hexagonal structure in graphite. It was found that the most convenient for estimating the amount of rhombohedral structure are reflexes $\left(10\frac{2}{3}\right)$ and (*101*). The differences in the rhombohedral modification between the individual samples of graphites are due to their morphological features. They can also be related to the mode of occurrence and different metamorphic environments of graphites.

INTRODUCTION

The occurrence of the rhombohedral form within the hexagonal structure in graphites has not yet been determined unequivocally. There is still controversy with regard not only to the presence of this form or its quantitative amounts in the structure of graphites but also to the mechanism of production of the rhombohedral modification in natural and industrial graphites. Thus, for example, Lipson and Stokes (1942) — who were the first to conclude that weak, additional reflections in powder X-ray photographs of graphite, inconsistent with the hexagonal structure, were due to the rhombohedral form — recorded a great concentration of this phase in graphite sample from Ceylon. In the same material Laves and Baskin (1956), Boehm and Hofmann (1955) and Freise and Kelly (1963) did not detect the rhombohedral form. They made numerous experiments as a result of which they established that the rhombohedral modification can be produced by unidirectional pressure associated with some shear or gliding. Their experiments on the thermal stability of the rhombohedral modification revealed that this is unstable and reverts to the hexagonal

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structure. The authors of the presented ideas carried out their investigations by means of the Buerger precession X-ray camera for the single crystal work and an X-ray diffractometer for the powder work.

In the case of industrial graphites (Oleś *et al.* 1975) it was found that in weakly graphitized materials the amount of the rhombohedral modification is fairly large (even 22 per cent). The unstable rhombohedral phase disappears as the degree of graphitization increases.

Lately very interesting papers (Diessel and Offler 1975, Hamilton *et al.* 1970, Landis 1971) have also appeared relating to the dependence between the structure of graphites or graphitized phytoclasts and the degree of metamorphism. In these publications the following methods are involved: X-ray technique, electron diffraction, differential thermal analysis and microscopic reflection measurements. The neutron diffraction method has not been used.

In our report we attempted to explain the occurrence of the rhombohedral structure in natural graphites by means of the neutron diffraction patterns. An effort was made to find and establish the relationship between the percentage of the rhombohedral phase and the morphological features and mode of occurrence of graphites and their geological conditions.

In order to investigate this the following five samples of graphites were chosen:

1) a massive specimen from the Pinerolo deposit (Italy),
2) dense chips from the Male Vrbno deposit (Czechoslovakia),
3) flakes (flinz type) from Passau (Germany),
4) flakes from the Ticonderoga — Lead Hill deposit (USA),
5) lumps from the Sri Lanka deposit.

The individual samples have a different shape, form, various grain sizes, crystallinity and different lustre and other macroscopic features. They represent different kinds and grades of metamorphism of the host rocks. Their characteristics are given in Table 1.

METHOD

The neutron diffraction method does not require any special preparation or mechanical treatment of samples. It by no means destroys the crystal structure, which sometimes occurs when an X-ray measurements are applied. The samples can be some cm^3 in volume and they are more representative for the whole material. Using the monochromatic neutron beam reflexes are obtained whose shapes depend only on the structural properties of the sample. Therefore from the profile of the experimental line the contribution of the rhombohedral phase can be determined. This is important because the reflexes of the two structures lie at the same Bragg angle or overlap.

The contribution of the rhombohedral structure is given by Kajzar (in press):

$$R = \frac{1}{\frac{I^{exp}_{H,hkl}}{I^{exp}_{R,hkl}} \cdot \frac{I^{th}_{R,hkl}}{I^{th}_{H,hkl}} + 1} \qquad [1]$$

where:

R — percentage of total mass of sample which has crystallized in the rhombohedral phase, (Kajzar in press),

$I^{exp}_{R,hkl}$ $I^{exp}_{H,hkl}$ — total measured intensity of the rhombohedral and hexagonal reflexes (hkl) respectively,

$I^{th}_{R,hkl}$ $I^{th}_{H,hkl}$ — total measured intensity of the rhombohedral and hexagonal reflexes (hkl) calculated from corresponding theoretical formulas for intensity of diffracted neutron or X-ray beam.

The relation: is well known:

$$\frac{I^{th}_{R,hkl}}{I^{th}_{H,hkl}} = \frac{(j_{hkl} \cdot F^2_{hkl} \cdot L_{hkl(\Theta)} \cdot A_{hkl(\Theta)}\, e^{-2W(\Theta)})_R}{(j_{hkl} \cdot F^2_{hkl} \cdot L_{hkl(\Theta)} \cdot A_{hkl(\Theta)}\, e^{-2W(\Theta)})_H} \qquad [2]$$

where:

j_{hkl} — multiplicity of the (hkl) reflex,
F_{hkl} — structural factor,
$W(\Theta)$ — Debye-Waller factor,
$L_{hkl(\Theta)}$ — Lorentz factor,
$A_{hkl(\Theta)}$ — absorption coefficient.

Indices R and H here and elsewhere denote the value for the rhombohedral or hexagonal reflexes.

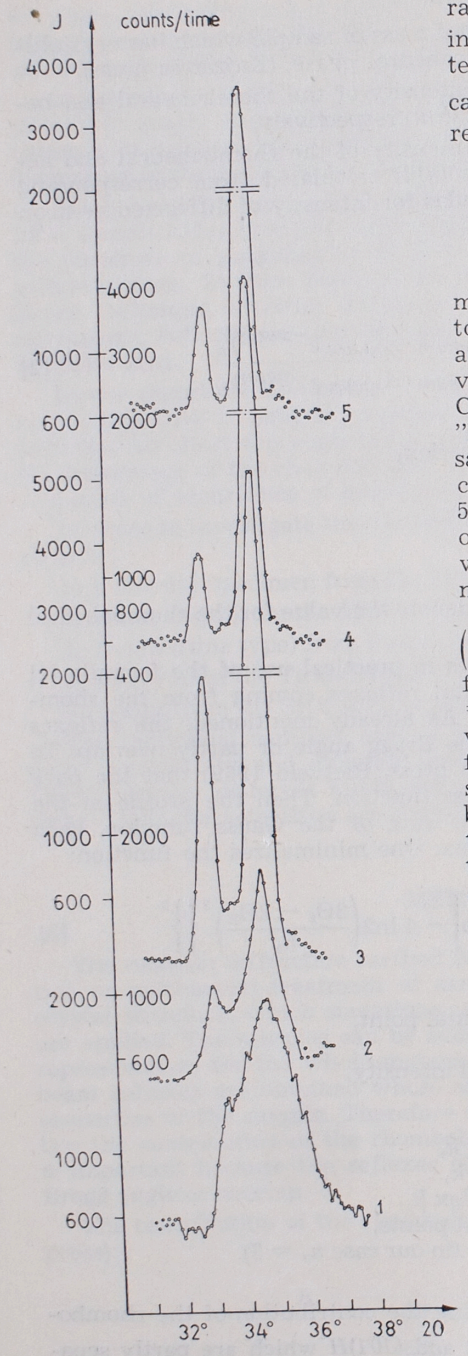
The greatest problem which arises in practical use of the formula [1] is that of separating the experimental reflexes coming from the rhombohedral and hexagonal structures. As already mentioned, the reflexes for the two structures lie at the same Bragg angle or partly overlap. To separate them we assume (Kajzar in press, Rietveld 1969) that the pure reflex can be described by the Gauss function. Then the profile of the experimental line is adjusted by the sum of the Gauss function, each corresponding to an overlapping reflex. One minimalizes the function:

$$x^2 = \sum_{i=1}^{n} W_i \left\{ D_i - \sum_{k=1}^{n_s} U_k \exp\left[-4 \ln 2 \left(\frac{2\Theta_i - 2\Theta_k}{b_k} \right)^2 \right] \right\}^2 \qquad [3]$$

where:

W_i — weight of its experimental point,
$W_i = 1/N_i + N_b$,
N_b — normalized background intensity,
N_i — measured intensity,
$D_i = N_i - N_b$,
U_k — amplitude of the reflex k,
b_k — halfwidth of the reflex k,
Θ_k — Bragg angle for the reflex k,
n — number of experimental points,
n_s — number of components (in our case $n_s = 3$).
$i = 1 \ldots n$.

The most convenient for determining the contribution of the rhombohedral structure are reflexes $\left(10\frac{2}{3}\right)R$ and $(101)H$ which are partly sepa-



rated, reflex $\left(10\frac{2}{3}\right)$ R being relatively intensive. In this case we have to determine 9 unknown parameters because $\left(10\frac{2}{3}\right)$ R is partly overlapped by reflex $(100)H$ (in formula [3] $n_s = 3$).

EXPERIMENTAL

The neutron diffraction measurements were performed on the diffractometer of the Institute of Physics and Nuclear Techniques of the University of Mining and Metallurgy in Cracow and installed at the reactor "Ewa" in Świerk. The investigated samples were placed in a vanadium container in diameter 15 mm and 50 mm high and mounted in the axis of the neutron diffractometer. This was done very carefully to avoid any mechanical stress.

To obtain the reflexes $(100)H$ $\left(10\frac{2}{3}\right)$ R, and $(101)H$ the neutron diffraction patterns for the angles $2\Theta = 27—43°$ were taken (neutron wavelength = 1,19 Å). The neutron diffraction patterns for the investigated samples are shown in Figure 1. It can be seen that there is the greatest contribution of the rhombohedral structure in the case of Pinerolo graphite and the smallest in that of Sri Lanka graphite.

RESULTS AND DISCUSSION

Using the Kajzar (in press) program, all the unknown parameters of equation [3] assuring a minimum of x^2 value were determined. The numerical calculations were performed on the Odra 1304 computer. The total intensities of $\left(10\frac{2}{3}\right)$ R and $(101)H$ were calculated and then from formula [1] the amount of the rhombohedral modification for each sample was established. In Figures 2 and 3 the refinement of the method is exemplarily shown for Czechoslovakian graphite. The quantitative results of the rhombohedral structure of the investigated graphites are given in Table 1.

As can be concluded from the experiments reported here, the quantitative contribution of the rhombohedral modification depends on the cry-

Fig. 1. The neutron diffraction patterns of natural graphites derived from the following deposits:
1 — Pinerolo (Italy), *2* — Male Vrbno (Czechoslovakia), *3* — Passau (West Germany), *4* — Ticonderoga (USA), *5* — Sri Lanka (Cejlon, Azja)

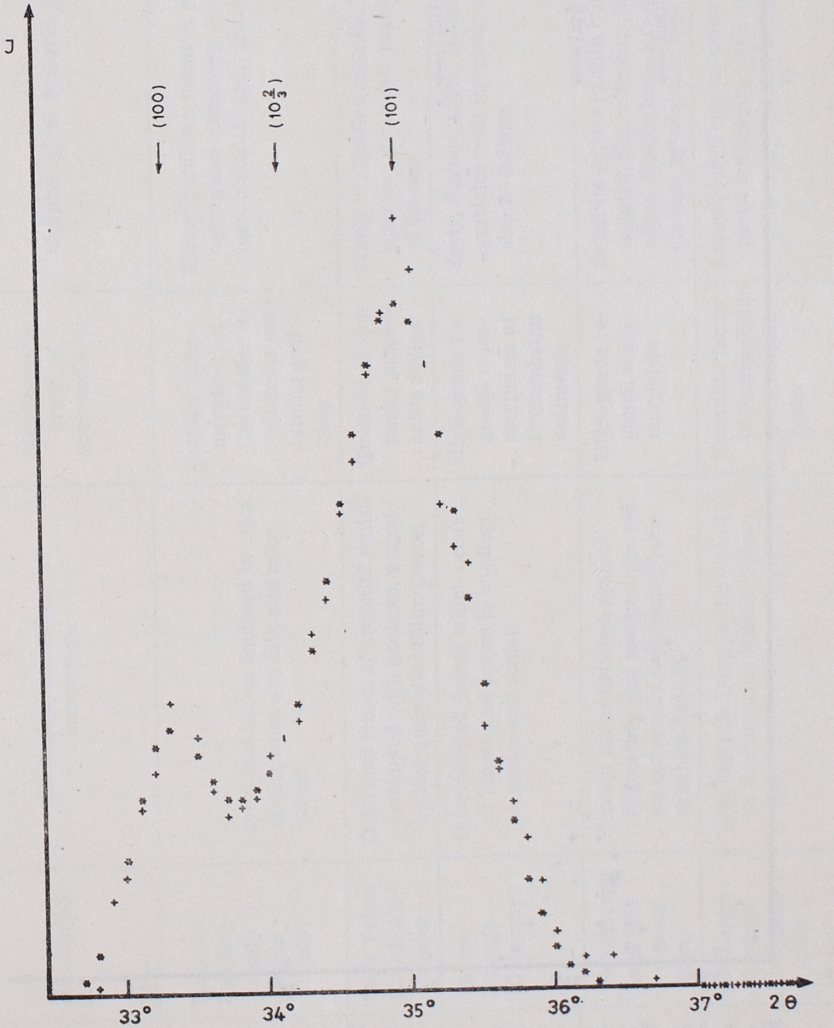


Fig. 2. The example of adjustment by means of the least squares method of theoretical line (*) to profile of the diffractional, experimental line (+)

stalline form of the graphites. The more perfectly crystalline is the form of graphite the smaller is the amount of the rhombohedral structure, e.g. well developed specimens from Ticonderoga and Sri Lanka deposits contain only three and two per cent of the rhombohedral phase, respectively. (Fig. 1, Tab. 1 — sample's No 4 and 5).

It is inferred that such differences in the rhombohedral modification are due to the different metamorphic environments in which the five graphites formed. The detection and identification of the amount of the

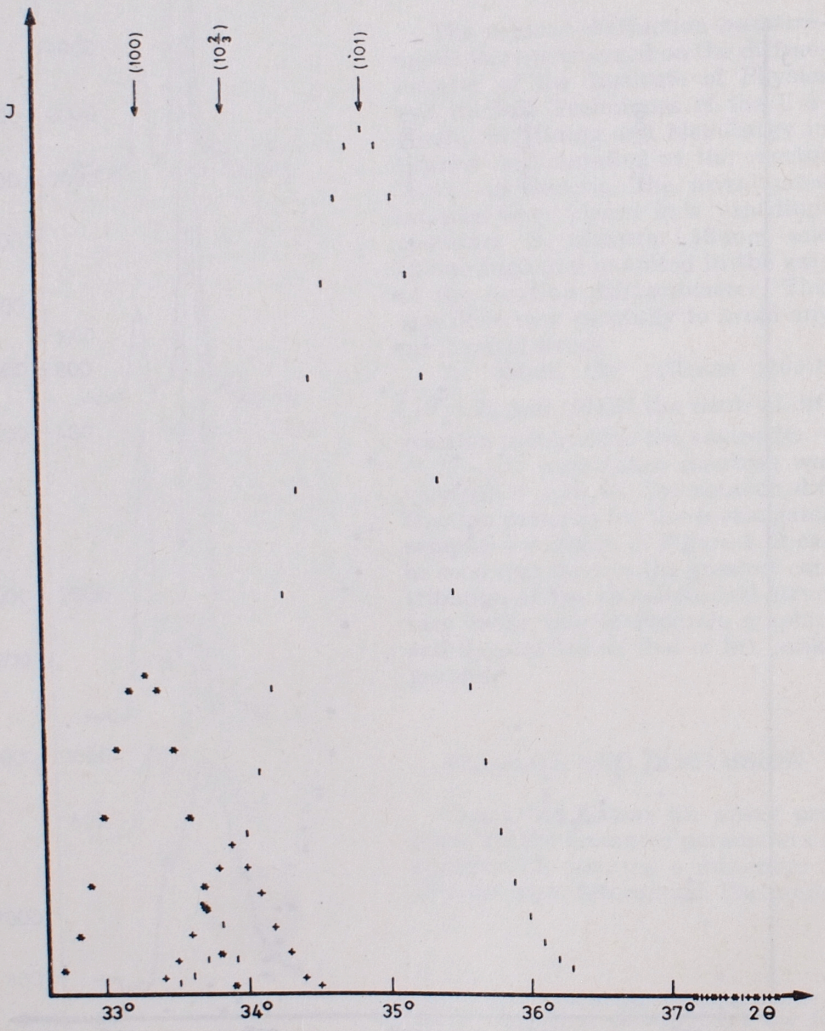


Fig. 3. The separating of the (100)*H*, $\left(10\frac{2}{3}\right)$ *R* and (101)*H* reflections for Male Vrbno graphite is exampled

Table 1

General characteristics of natural graphites

No	Locality	Geological conditions of occurrence	Metamorphic grade of environments	Morphological features of graphites	Amount of rhombohedral phase (*R* %)
1	Pinerolo San Germano mine (Italy)	Layers and lenses enclosed in mica gneiss, mica phyllite and mica schist	Contact metamorphism of Carboniferous sediments containing coal beds	Microcrystalline, massive, occur in dull aggregates extremely fine-grained texture, blackish-grey, grain size < 0,1 mm	25
2	Male Vrbno (Czechoslovakia)	Deformed lenses of graphite schist associated with gneisses, amphibolites quartzites/Silur-Devon	Greenschist and partly amphibolite facies	Finely crystalline metallic lustre, distinct schistose structure, particle size < 0,5 mm	11
3	Passau Bavaria (Germany)	Disseminated flakes which occur in lenses and seams in cordierite gneiss and schist	High-grade regional metamorphism of Precambrian sediments	Scaly, fibrous, black, lustrous plate-like particles with irregular edges, crystal size 2—0,5 mm	9
4	Ticonderoga Lead Hill deposit (USA)	Contact zones between granitic pegmatites and metamorphosed carbonaceous sediments Flake graphite deposit	High-grade regional metamorphism	Graphite occurs in thin but large plates, isolated, flat with angular and rounded edges. Flakes have a perfect basal clevage, crystal size 5—1 mm	3
5	Sri Lanka (Ceylon) Medapola mine (Asia)	Vein deposits lying in the vicinity of Precambrian igneous intrusions	Granulite facies of Precambrian metamorphic rocks	Lumps, large crystal pieces, sharp-cornered fragments, pure, coarsely crystalline crystal size > 10 mm	2

rhombohedral structure in some natural graphites are thus of particular importance for crystallographical studies. It is suggested that the neutron diffraction technique is a more suitable in this application than the X-ray method.

REFERENCES

BOEHM H. P., HOFMANN U., 1955: Die rhomboedrische modifikation des Graphites. *Z. anorg. allg. Chem.* 278.

DIESSEL C. F. K., OFFLER R., 1975: Change in physical properties of coalified and graphitised phytoclasts with grade of metamorphism. *N.Jb. Miner. Mh.* H. 1.

FREISE E. J., KELLY A., 1963: The deformation of graphite crystals and the production of the rhombohedral form. *Phil. Mag.* 3.

HAMILTON L. H., RAMSDEN A. R., STEPHENS J. F., 1970: Fossiliferous graphite from Undercliff, New South Wales. *J. Geol. Soc. of Australia*, vol. 17.

KAJZAR F., (in press): A profile refinement method for determination of the contribution of rhombohedral structure in graphites. Report of the Institute of Physics and Nuclear Techniques, Cracow.

LANDIS C. A., 1971: Graphitization of dispersed carbonaceous material in metamorphic rocks. *Contr. Mineral. and Petr.* 30.

LAVES F., BASKIN Y., 1956: On the formation of the rhombohedral graphite modification. *Zeitschrift für Kristallographie.* 107, 5/6.

LIPSON H., STOKES A. R., 1942: The structure of graphite. *Proc. Roy. Soc. A* 181, 93.

OLEŚ A., KAJZAR F., NIZIOŁ St., PAWŁOWSKI K., WŁODARCZYK Z., 1975: Neutronograficzna metoda wyznaczania bezwzględnego stopnia zgrafityzowania oraz udziału struktury romboedrycznej. *Zesz. nauk. AGH*, 483.

RIETVELD M. M., 1969: A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.* 2, 65.

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UDZIAŁ STRUKTURY ROMBOEDRYCZNEJ W GRAFITACH NATURALNYCH OKREŚLONYCH METODĄ NEUTRONOGRAFICZNĄ

Streszczenie

W niniejszej pracy wykorzystano metodę dyfrakcji neutronów do zbadania ilościowego udziału fazy romboedrycznej występującej w obrębie struktury heksagonalnej w grafitach. W tym celu wybrano do badań pięć próbek grafitów naturalnych pochodzących z następujących złóż: Pinerolo, Male Vrbno, Passawa, Ticonderoga, Sri Lanka. Poszczególne próbki różniły się między sobą formą wykształcenia, wielkością kryształów, połyskiem oraz reprezentowały różne facje metamorficzne.

Pomiary neutronograficzne wykonano na dyfraktometrze Instytutu Fizyki i Techniki Jądrowej AGH zainstalowanym przy reaktorze „Ewa" w Świerku. Stosując monochromatyczny strumień neutronów otrzymano refleksy których kształty zależały jedynie od strukturalnych własności próbek. Najbardziej dogodne dla określenia struktury romboedrycznej okazały się refleksy $\left(10\frac{2}{3}\right)$ R i $(101)H$. W celu rozdzielenia tych refleksów

założono, że kształt może być opisany funkcją Gaussa. Następnie metodą najmniejszych kwadratów do profilu linii dyfrakcyjnej dopasowywano sumę funkcji Gaussa odpowiadających poszczególnym refleksom. Obliczenia numeryczne przeprowadzono na maszynie cyfrowej Odra 1304. Wyliczono całkowite natężenia refleksów $\left(10\frac{2}{3}\right)$ i (101) oraz określono udział modyfikacji romboedrycznej dla każdej próbki.

Uzyskane wyniki wskazują na pewne zależności procentowej zawartości fazy romboedrycznej od stopnia wykrystalizowania próbek. Im bardziej doskonała forma krystalograficzna grafitu oraz silniejszy stopień metamorfizmu skał otaczających dane złoże, tym mniejsza jest zawartość fazy romboedrycznej.

OBJAŚNIENIA FIGUR

Fig. 1. Neutronogramy grafitów naturalnych pochodzących z następujących złóż: *1* — Pinerolo (Włochy), *2* — Male Vrbno (Czechosłowacja), *3* — Passawa (Niemcy), *4* — Ticonderoga (Stany Zjednoczone Ameryki Północnej), *5* — Sri Lanka (Cejlon—Azja)

Fig. 2. Przykład dopasowania metodą najmniejszych kwadratów linii teoretycznej (*) do profilu dyfrakcyjnej linii doświadczalnej (+)

Fig. 3. Przykładowe rozdzielenie refleksów $(100)H$, $\left(10\frac{2}{3}\right)R$ i $(101)H$ dla grafitu Male Vrbno

Барбара КВЕЦИНЬСКА, Францишек КАЙЗАР

РОЛЬ РОМБОЭДРИЧЕСКОЙ СТРУКТУРЫ В СТРОЕНИИ ПРИРОДНЫХ ГРАФИТОВ, ОПРЕДЕЛЕННАЯ НЕЙТРОНОГРАФИЧЕСКИМ МЕТОДОМ

Резюме

Использовался метод дифракции нейтронов для количественного определения объема ромбоэдрической фазы в гексагональной структуре графитов. Исследования проводились на пяти образцах графитов из месторождений Пинероло, Мале-Врбно, Пассава, Тикондерога и Сри-Ланка. Графиты из этих месторождений отличались друг от друга чертами строения, величиной кристаллов, блеском и представляли разные стадии метаморфизма.

Нейтронографические определения производились на дифрактометре Института ядерной физики и техники Горно-Металлургической академии установленном у реактора „Ева" в Сверке. Применением монохроматического потока нейтронов были получены рефлексы, формы которых соответствовали единственно структурным свойствам образцов. Наиболее пригодные для определения ромбоэдрической структуры оказались рефлексы $(10\frac{2}{3})R$ и $(101)H$. С целью разделения этих рефлексов было принятно, что форму можно описать с помощью функции Гаусса. Затем методом наименьших квадратов сопоставлялись с профилем дифракционной линии суммы функций Гаусса, соответствующих отдельным ре-

флексам. Вычисления произведились на ЭВМ Одра 1304. Получены полные интенсивности рефлексов и определено количество ромбоэдрической модификации во всех образцах.

Полученные данные выявляют определенную зависимость содержания ромбоэдрической фазы от степени кристаллизации. Чем более совершенна кристаллографическая форма графита и более сильная степень метаморфизма вмещающих пород, тем меньше количество ромбоэдрической фазы.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Нейтронограммы природных графитов из разных месторождений:
1 — Пинероло (Италия), *2* — Мале-Врбно (Чехословакия), *3* — Пассава (Германия), *4* — Тикондерода (США), *5* — Сри Ланка (Цейлон)

Фиг. 2. Пример сопоставления методом наименьших квадратов теоретической линии (—) с профилем дифракционной экспериментальной линии (+)

Фиг. 3. Пример разделения рефлексов $(100)H\left(10\frac{2}{3}\right)R$ и $(101)H$ графита из месторождения Мале-Врбно