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AN ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF CEMENTITE

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The crystal structure of cementite, separated from annealed carbon steel by anode solution, was investigated by electron diffraction. From hk0 zone reflections a projection of the potential on the (001) plane was constructed, allowing the $\underline{x}$ and $\underline{y}$ coordinates of the Fe and C atoms to be determined. The results obtained confirm the position of Fe given in earlier papers, and show that the C atom does not lie in a general position in a trigonal prism, as suggested by Westgren, Lipson, and Petch, but in the octahedral hole (in the 000 position).

The structure of cementite was first studied by Westgren and Phragmen [1], using x-ray methods on a powder separated from carbon steel containing 1.25% C, and they found that the cementite lattice had the following parameters $a = 4.517$, $b = 5.079$, $c = 6.730$ kX. On the basis of these results, Hendriks [2] determined the space group (Pbnm) and the positions of the iron atoms. As regards the carbon atoms, he suggested (without trying to use reflection intensities to support this) that these might lie in the octahedral holes (in the positions 000, $00{}^1/_2$, ${}^1/_2{}^1/_2 0$ and ${}^1/_2{}^1/_2{}^1/_2$). Subsequently, Westgren [3] confirmed the positions for the iron atoms found in [2], but considered that Hendriks' proposed carbon atom positions were unlikely, since if the atoms were placed in the octahedral holes the carbon atom radius would have to be less than that normally found in the carbides WC, TiC, VC. From geometrical considerations Westgren favored the possibility of the carbon atoms lying in trigonal prisms, which are of larger volume than the octahedral holes. Although experimental and calculated intensities were in good agreement in this case, Westgren considered that the weak x-ray scattering shown by the carbon atoms was insufficient for complete confirmation of the carbon atom positions in the cementite lattice.

Lipson and Petch [4] carried out an x-ray structural analysis on cementite prepared by the reduction of ferric oxide in a stream of CO at 550°. With this method of preparing cementite it is necessary to check the purity of the product. It is essential that this does not contain remnants of ferric oxide or oxygen in any form. Unfortunately the specimens were not checked for oxygen content, and so there is no proof that this impurity, which could appreciably affect the observed intensities, was absent.

On the x-ray photos of the prepared cementite, the authors observed 30 diffuse lines. Annealed powder gave a sharper x-ray pattern, but at the same time annealing at temperatures above 600° led to partial breakdown, with the separation, in the authors' opinion, of the carbide Fe_2C. Therefore, the intensities of reflections were measured from the x-ray photos of unannealed specimens, and the interplanar distances from specimens annealed at 600°.

In the paper, Westgren's conclusions [3] were confirmed in principal.

In the cementite structure, therefore, the space group, lattice parameters, and iron atom positions were reasonably reliably established. The available experimental data did not allow the proposed carbon atom arrangement to be investigated further with more assurance. The purpose of the present work is to locate the C atoms in the cementite lattice, using electron-diffraction structural analysis.

Experimental Method

In this investigation cementite from annealed carbon steel of the following composition was used: C-0.79%, Mn-0.34%, Si-0.24%, P-0.014%, and S-0.013%.

In preparation of the electron-diffraction patterns the cementite particles were separated from the steel specimens by anode solution, and after washing were placed on a gauze in a collodion mounting. The electrolyte used was 5% iron chloride solution in methylated spirits containing 2% citric acid [5].

Investigation of the precipitate was carried out using the ÉM-4 electron beam instrument. The cementite powder gave distinct rings (which were, however, made up of separate reflections) on the photos.

In order to give rings of uniform blackening, the specimen was continuously rotated during photographing.

The intensities of the reflections were measured on the MF-4 photomicrometer. To increase the sensitivity the photomicrometer was supplemented with a radiometric circuit containing an electronic potentiometer which amplified the current from the photoelement and transformed it logarithmically [6]. Using the electronic potentiometer for recording the photometric curves, and the logarithmic transformation of the photoelement current increased many times the accuracy of measurement of the weak reflections. The accuracy of measurement of the strong and medium reflections was about 3%, and that of the weak reflections of the order of 15%. The intensity of each reflection was determined from the average of five measurements on different photos. The average difference in intensities on different photos varied between ± 5%.

This method also allowed a more accurate determination of the diameter of the diffraction ring, and consequently of the interplanar distances. For recording the photometric curves the photos were enlarged 10 times. In calculation of the interplanar distances an electron-diffraction photo of pure sodium chloride was used. The error in this determination did not exceed 0.003 A.

The photos normally had a considerable background which rapidly diminished from the center of the plate outwards. For accurate determination of intensities it is necessary to take this feature into account somehow. In the present work this was done by photometry of pure collodion films exposed for various periods, and superimposition of the background on the cementite electron-diffraction photo. The superimposition allowed better determination of the background lines in places where several strong reflections were in very close proximity to each other.

Experimental Results

Electron-diffraction photos taken at an angle showed that the specimens were strongly textured, and it was not possible to obviate this by prolonged grinding in an agate mortar. Spheroidizing annealing was also unsuccessful. After annealing, cementite spheroids of diameter 0.5-4 μ were formed, and these gave photos with a strong background, which obscured a large number of weak reflections and even some medium ones. It was therefore necessary to use specimens with a plate-like texture. On the photos, however, all cementite reflections were observed because the plates were not absolutely horizontal and had some angular spread.

On the electron-diffraction photos made, 125 reflections were established (Fig. 1), which were indexed on the basis of an orthorhombic lattice. It was established that the hk0 reflections were all present, and systematic absences of the h0l reflections with $h + l \neq 2n$ and the 0kl reflections with $k \neq 2n$ were observed, which confirmed the space group D_{2h}^{6}-Pbnm. The unit cell dimensions found in this investigation were in full agreement with those of [1].

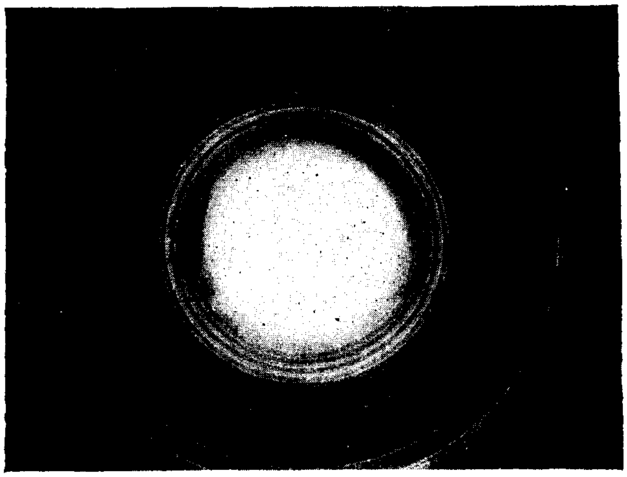

Fig. 1. Electron-diffraction photo of cementite particles separated from annealed carbon steel.

On the electron-diffraction photos there were some quite intense forbidden h00, 0k0, 00l reflections with odd *h*, *k*, and l, particularly apparent on the point electron-diffraction photos (Fig. 2), which were made on an electron microscope using the microdiffraction method.*

Analysis of oblique texture photos and point electron-diffraction patterns supported the conclusion that the cementite plates were disposed with their (001) faces parallel to the surface of the mounting. Because of this texture, the projection of the potential on the (001) plane could be constructed from the hk0 zone reflections, and the *x* and *y* coordinates of iron and carbon found. Determination of the *z* coordinates under these conditions is extremely difficult.

The reflection intensities were measured on photos taken perpendicular to the beam. Generally speaking, the measurements are best carried out on photos of the oblique texture kind, on the zero layer line of which only the hk0 reflections appear. However, on these photos the background was much more intense, obscuring the weak reflections. In addition, under our conditions the zero layer line ran along the short side of the photographic plate, so that on the oblique texture photos only reflections with d = 1.125 A were defined, and on the photos taken perpendicular to the beam, only those with d = 0.790 A.

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* The point electron-diffraction photos were prepared in the Crystallography Institute of the Academy of Sciences, USSR, by N. A. Kiselev and Yu. P. Borozdin, to whom the author expresses his very grateful thanks for this assistance.

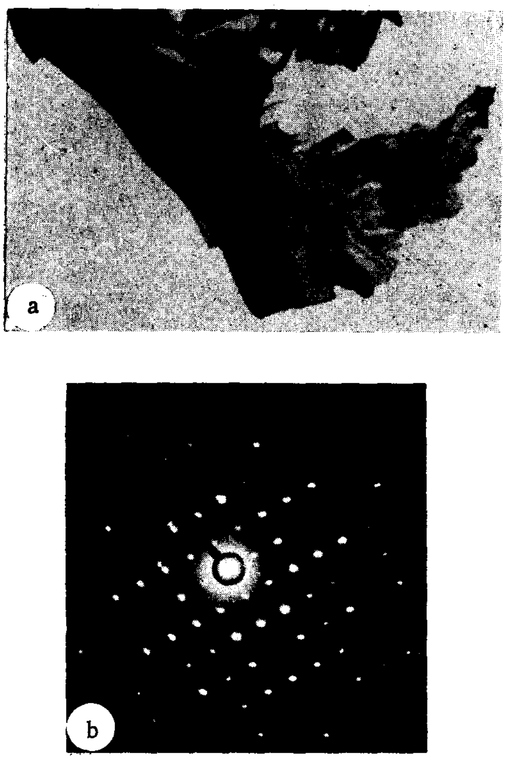

Fig. 2. Electron photomicrograph (a) and point electron-diffraction pattern (b) of a cementite particle.

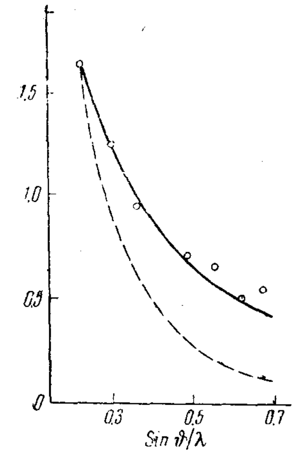

Fig. 3. Electron scattering curves. Continuous line) f; dashed line) f^2; circles) I/pd^2.

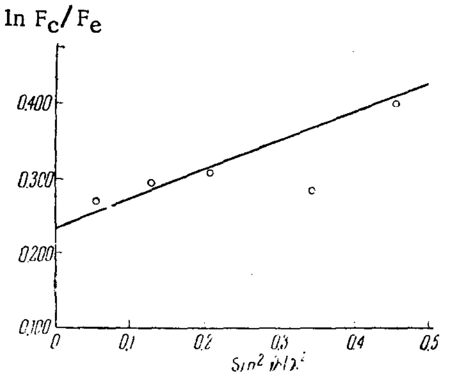

Fig. 4. Graph for determination of normalizing coefficient and temperature correction.

In any event, on several of the oblique texture photos the intensities of the reflections present were measured. A comparison of these with intensities on photos taken perpendicular to the beam showed that these did not differ by more than 10%.

In calculation of the structure amplitudes it was necessary to examine the nature of the electron scattering. In an earlier work [7] it was established that in perlite, formed by isothermal quenching at 700°, the cementite plates have an average thickness of the order of 1700 A. We may therefore expect that the electron scattering would have a dynamic character, and this is confirmed by a comparison of the average values of I/pd^2 plotted aginst $\sin \vartheta/\lambda$ with the f and f^2 curves for iron according to [8] (Fig. 3). Here the step from the observed intensities to the structure amplitudes was made according to the formula [8]

$$F_{hkl} = \frac{I_{hkl}}{d^2_{hkl}\, p},$$

where p is the recurrence factor for the texture. In the cases where hk0 reflections coincided in one ring with reflections of different index, the intensities were shared out proportionately to the intensities on the point photo, where each reflection was observed separately. If hkl reflections coincided in the same ring, their intensities were found by calculating them and multiplying by the coefficient 0.52. This coefficient was derived from the ratio of the sum of experimental intensities in the hkl reflections observed separately to the sum of calculated intensities for these reflections.

The experimental amplitudes found were normalized to volts by a method proposed by Vainshtein [8], and by a comparison of the change of $\ln F_c/F_e$ with $\sin^2 \vartheta/\lambda^2$ [9] (Fig. 4). Both methods gave closely similar normalizing coefficients (spread not exceeding 3%).

From the slope of the straight line in Fig. 4 the temperature correction was found. The value of B was found to be 0.5. Using this value of B the calculated amplitudes were corrected and the normalizing coefficient recalculated. The values derived are shown in Table 1.

Fourier Potential Synthesis

From the experimental values of the cementite reflections a Fourier synthesis of the potential on the (001) plane was constructed. The signs of the amplitudes were calculated from the atomic coordinates found by Westgren, using refined values of the atomic factors [10, 11]. The projection of the potential is shown in Fig. 5, where

TABLE 1. Experimental and Calculated Values of the Amplitudes F_{hk0} (in V)

$hk0$	F_c	F_e	$hk0$	F_c	F_e
110	+1.81	0.17	150	+0.04	0.17
020	+1.26	1.66	340	+0.02	0.46
200	−4.70	4.70	430	−0.60	0.39
120	−4.55	4.15	250	−1.16	0.93
210	+6.47	6.70	510	+0.83	0.72
220	+0.83	0.60	520	+1.30	1.39
130	+4.97	4.20	060	+3.00	4.00
310	+0.93	1.07	440	+0.71	1.03
230	+0.79	0.57	350	+1.00	3.23
320	−0.48	0.55	160	+0.71	1.65
040	+0.36	0.88	530	+1.64	1.08
140	+4.26	3.90	260	−0.80	1.09
400	−1.96	2.02	450	+0.49	0.76
330	−4.37	3.94	600	+2.78	3.13
240	+0.46	0.47	610	−0.14	0.35
410	−2.70	2.35	360	−0.28	0.06
420	+1.11	0.97	540	−1.79	1.22

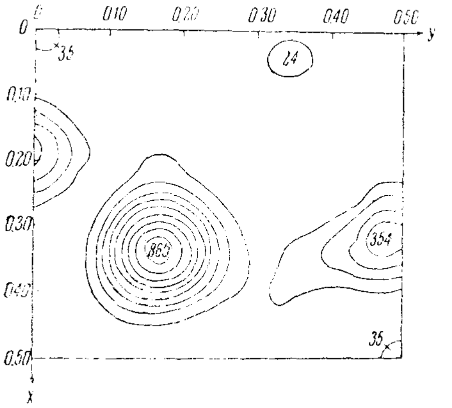

Fig. 5. Potential projection of cementite on the (001) plane. The lines of equal value are at 100 V-A intervals. Figures inside the lines indicate maximum values of the peak potentials.

the peaks due to the iron atoms are prominent. It does not appear possible from this to settle the position of the carbon atom undisputedly. There are on the projection two small peaks; one at the origin of coordinates, and the other at the position $x_3 = -0.46$, $y_3 = 0.155$. The position of the iron atom differs a little from that given in [3, 4].

After conversion of the signs of the amplitudes the potential projection was again constructed, and on this the peak at the origin had disappeared, and the other peaks were somewhat displaced. The magnitude of the small peak fell to 10 V-A here.† So this projection as well does not allow the carbon atom position to be defined, since from calculations in [8] the projection potential of a carbon atom should be 145 V-A. Construction of a third projection seemed unjustified, since the signs of the structure amplitudes calculated from the new coordinates were unchanged. Although the results threw some doubt on the correctness of the original premise, the investigation was nonetheless pursued using a Fourier synthesis. To obviate the effect of the heavy atoms a difference projection was constructed from the formula [12]

$$F_{Fe_e} = Fe \cdot (F_{Fe_c}/F_c)$$

and by dividing by the appropriate trigonometrical factor (Fig. 6).

On this projection a small peak was again detected at the origin, and there was a marked shift of the second peak, the position of which had remained almost unchanged in the first two projections. However, the height of this peak was small, as before, so that it could not be taken as the carbon peak.

This part of the investigation, therefore, did not confirm the arrangement of carbon atoms in general posi-

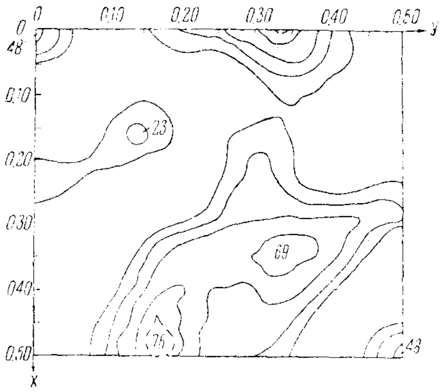

Fig. 6. Difference projection of the potential of cementite on the (001) plane. Solid lines are at 20 V-A intervals, dashed lines at 10 V-A intervals.

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† Here V-A stands for volt-angstrom units.

TABLE 2. Atomic Positions of Iron and Carbon

Atom	Coordinates	Hendriks [2]	Westgren [3]	Lipson and Petch [4]	This paper
8 Fe	x_1	0.340	0.333	0.333	0.338
	y_1	0.170	0.185	0.183	0.169
	z_1	0.065	0.065	0.065	–
4 Fe	x_2	−0.160	−0.167	−0.167	−0.178
	y_2	0.050	0.040	0.040	0.030
	z_2	0.250	0.250	0.250	–
	x_3	–	0.430	0.470	0
	y_3	–	−0.130	−0.140	0
	z_3	–	0.250	0.250	–

tions, as found in [3] and [4]. Fourier potential projections were therefore constructed on the basis that the carbon atom lay in the octahedral hole, i.e., at the origin of coordinates.

The first projection was constructed with the iron atom coordinates found by Westgren, and this showed unambigously that the carbon atom lay at the origin. The iron atom peaks lay at the same positions as in the first projection constructed (Fig. 4). A second calculation of the structure amplitude signs from the new iron atom coordinates, and construction of another projection indicated a small change in the positions of the iron atoms, but the carbon atom peak was not shifted from the origin (Fig. 7). In a further calculation the signs of the structure amplitudes were unchanged. The final values for the atomic coordinates, together with those of other authors, are shown in Table 2. The positions of the peaks were calculated according to Booth's method.

The mean-square error in determination of the iron atom coordinates, according to calculations in [8], was 0.001 A.

A comparison of experimental and calculated structure amplitudes is shown in Fig. 8 which indicates that experimental results correspond much better with those

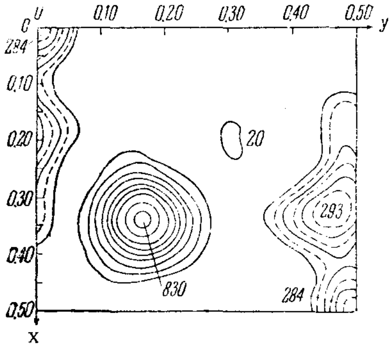

Fig. 7. Potential projection of cementite on the (001) plane. Solid lines are at 100 V-A intervals, dashed lines at 50 V-A intervals.

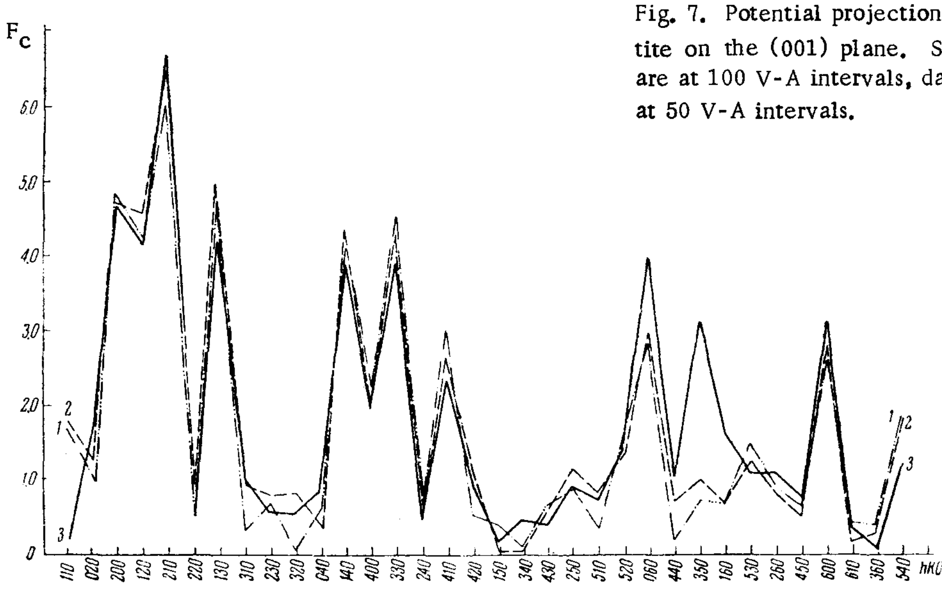

Fig. 8. Comparison of calculated and experimental amplitudes. 1) Values calculated for carbon atoms lying in a trigonal prism (according to Westgren); 2) values calculated for carbon atoms lying in octahedral holes; 3) experimental values.

calculated for the carbon atom lying in the octahedral hole. Rather more tangible support for this is provided by the values of the probability factor R. For the case of the carbon atom lying in the octahedral hole, R = 23.3%, and for in the prism, R = 27.2%. There is approximately the same ratio between the probability factors for the hk0 reflections taken separately, but for the C atom lying in the octahedral hole, R = 14.8%.

Discussion of Results

Figure 9 gives a general view of the structure of Fe_3C, and Fig. 10 shows the interatomic distances in the cementite molecule, calculated from the $\underline{x}$ and $\underline{y}$ coordinates found in the present work (the $\underline{z}$ coordinates are taken from Westgren). The average length of the Fe-C bond is 1.86 A, much less than the average value of 2.03 A found in [4], which appears to be exaggerated.

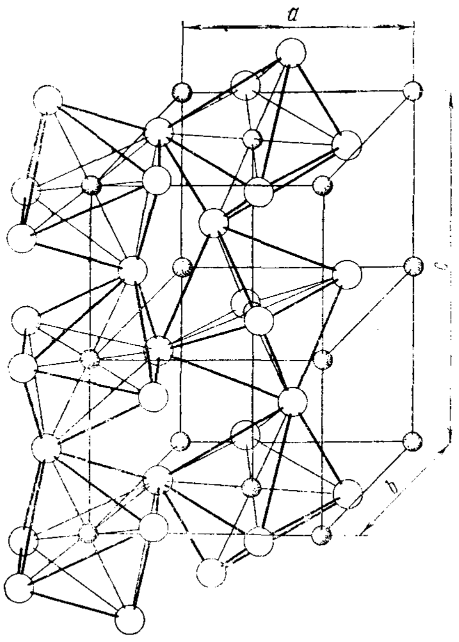

Fig. 9. Structure of cementite.

If we work out the length of the Fe-C bond in austenite, basing the calculation on the increase in lattice parameters with increasing carbon content, we get a value of 1.97 A. The decrease in length of this bond has been fully explained by work in recent years which has confirmed experimentally [13, 14] that the carbon in austenite lies in the octahedral holes, and is in an ionized state, behaving as a cation. Results available on the properties of austenite and cementite suggest that the Fe-C bond is stronger in cementite than in austenite. So the Fe-C bond length in cementite would not be greater than in austenite, it would on the contrary be expected to be less.

The Fe-C bond length is probably somewhat greater than 1.86 A, as a result of which the Fe atoms are slightly displaced from the ideal positions. This is supported, in particular, by the appearance of the forbidden reflections 100, 300, 500, 010, 030, and 050. These reflections can arise from the secondary scattering of electrons but in our case, if this does take place, it is on a small scale. A comparison of experimental and calculated intensities for the strongest reflections provides support for this view. If there was appreciable secondary scattering taking place, the calculated values would have to be greater than the experimental values. Our results show that this does not apply (Table 1). In addition, the intensities of reflections not referable to an orthorhombic lattice were not great enough to assume that significant secondary scattering was occurring.

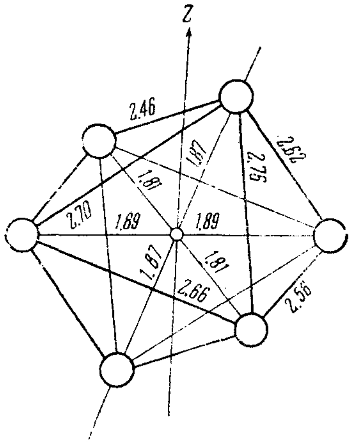

Fig. 10. Interatomic distances in the cementite molecule.

Conclusions

Using electron-diffraction methods, the structure of cementite was refined. It was established that the carbon atoms lie within octahedral holes.

In conclusion the author expresses very grateful thanks to B. K. Vainshtein for valuable advice and for great help in carrying this work out. The author thanks É. D. Furyaeva, who carried out the laborious Fourier synthesis calculations.

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