

A COMPARISON OF THE STRUCTURAL AND PHOTOLUMINESCENT PROPERTIES OF THE LUMINOPHORES ZnS—Cu, Cl

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The structural and photoluminescent properties of two groups of luminophores ZnS-Cu, Cl are compared with a constant Cu activator content and variable NaCl fluxing agent content and, conversely, with a constant NaCl content and variable Cu content. No changes in SnZ lattice constants related to the admixtures introduced or the method of luminophore production were found. In all the luminophores examined röntgenographically two phases were observed: sphalerite and wurtzite. It was found that if the content of both types of admixtures in the luminophores is low the wurtzite phase predominates, but when the amount of admixtures increases it gradually changes into the sphalerite phase.

1. Introduction

The photoluminescent properties of the luminophores ZnS—Cu, Cl depend on several factors, that is, mainly on the sintering technique and temperature, the method of introducing the activator and fluxing admixtures, their quantitative relations and on the temperature at which the tests are carried out [1–6]. On the other hand, changes in the admixture content result in changes in the structure of the luminophores investigated.

The aim of the investigations presented here was to compare the structural and photoluminescent properties of the luminophores ZnS—Cu, Cl.

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1. The luminophores ZnS-Cu, Cl were produced by sintering a mixture of the basic substance ZnS, the copper activator, and the fluxing agent NaCl at a temperature of $970 \pm 10^\circ\text{C}$ by the method described in [7], the so-called "usual" method.

They represent two groups:

I — with a constant activator, Cu, content and a variable fluxing agent, NaCl, content.

II — with a constant fluxing agent, NaCl, content and a variable activator, Cu, content. Moreover, one luminophore No. II 6a produced by the diffusive method of Cu incorporation, [1] and [2], was included in Group II.

According to D. Curie [8] the sintering temperature is approximately that of the complete change of the sphalerite phase into the wurtzite phase (1024°C). Therefore the structure of the luminophore samples investigated should be mixed, sphalerite-wurtzite.

The determinations of 8 samples on which X-ray examinations were made and their corresponding luminophores together with the admixture constitution are given in Table I.

TABLE I

Comparison of determination of samples and of corresponding luminophores, and their composition before sintering

Sample No.	Luminophor designation	Cu content	NaCl content	Sintering method
1	I—1	$4 \cdot 10^{-5}$	1%	simple
2	I—5	$4 \cdot 10^{-5}$	5%	simple
3	I—8	$4 \cdot 10^{-5}$	8%	simple
4	II—0	0	4%	simple
5	II—3	10^{-4}	4%	simple
6	II—5	10^{-3}	4%	simple
7	II—6	$2 \cdot 10^{-4}$	4%	simple
8	II—6a	$2 \cdot 10^{-4}$	4%	diffusive incorporation of additional copper

It contains the three most typical luminophores of Group I and five luminophores of Group II.

In order to study the structure of the luminophores powder, photographs were taken, with a Deby-Scherrer-Hull camera, 114.6 mm diameter, by means of the Straumanis method [9]. For the exposure Cu $K\alpha$ radiation with a nickel filtre was used. The measurements of the lines of interference were evaluated with an accuracy of ± 0.1 mm, with corrections made each time for the camera circumference. The measurements were made at a constant temperature of 23°C . The results of the measurements for the most typical samples are presented in Table II. The hkl indices of all the lines of interference on the röntgenograms are given, showing the sphalerite and wurtzite phases and the line resulting from the addition of NaCl to the sample. The intensity of the lines observed was evaluated visually using a 5-degree scale of comparison: v.s — very strong, s — strong, m. — medium, w. — weak, v.w. — very weak.

TABLE II

Results of röntgenographic analysis

No of the sample		1				3				7			
No	20	w. p. hkl	s. p. hkl	NaCl hkl	I	w. p. hkl	s. p. hkl	NaCl hkl	I	w. p. hkl	s. p. hkl	NaCl hkl	I
1	27.2	100		111	s.	100		111	s.	100		111	s.
2	28.7	002	111		v. s.	002	111		v. s.	002	111		v. s.
3	30.8	101			s.	101			s.	101			s.
4	31.9				—			200	v. w.			200	v. w.
5	33.2				—		200		a.		200		v. w.
6	39.6				a.	102			a.	102			a.
7	45.4				—			220	v. w.				—
8	47.7	110	220		v. s.	110	220		v. s.	110	220		v. s.
9	52.0	103			s.	103			s.	103			s.
10	56.6	112	311	222	v. s.	112	311	222	v. s.	112	311	222	v. s.
11	57.7	201			w.	201			w.	201			w.
12	59.2	004	222		v. w.	004	222		v. w.				—
13	63.6	202			v. w.	202			v. w.	202			v. w.
14	69.6		400		w.		400		w.		400		w.
15	73.2	203			a.	203			a.	203			a.
16	76.3			042	v. w.			042	v. w.			042	v. w.
17	77.1		331		a.		331		a.		331		a.
18	78.1	211			w.	211			w.	211			w.
19	79.3		420		v. w.		420		v. w.		420		v. w.
20	82.5	105		422	w.	105		422	w.	105		422	w.
21	88.7		422		s.		422		s.		422		s.
22	92.0	213			a.	213			a.	213			a.
23	95.8		333, 511		s.		333, 511		s.		333, 511		s.
24	101.4	205			w.	205			w.	205			w.
25	107.6		440		a.		440		a.		440		a.
26	115.0	222	531		s.	222	531		s.	222	531		s.
27	121.4	215			a.	215			w.	215			a.
28	128.8		620		w.		620		s.		620		w.
29	133.1	313			s.	313			w.	313			s.
30	137.7		533		w.		533		w.		533		v. w.
31	148.6			444	v. w.			444	v. w.			444	v. w.
32	162.9				—		444		s.		444		s.

2. Results and conclusions

As Table II shows, increasing concentrations of both the fluxing agent and of the activator causes changes in the intensity of the lines of interference particularly when the magnitude of the θ angle is high. The angles of the corresponding lines of interference do not differ in the various luminophore samples, therefore no changes in the ZnS lattice

structure in relation to the admixtures of the activator Cu and the fluxing agent NaCl added were noted. This is due to the following causes:

a) The magnitude of the ion radii of the admixtures incorporated into the crystalline lattice of the luminophores are similar to the ion radii of the basic substance ZnS. Copper becomes incorporated in the lattice in the form of a monovalent ion Cu^+ with a radius of (0.90 Å; 0.98 Å) replacing the bivalent Zn^{2+} ion with a radius of (1.31 Å; 0.83 Å) and the chlorine ion Cl^- with a radius of (1.84 Å) is incorporated in the place of the sulphur ion S^{2-} with a radius of (1.84 Å; 1.85 Å). These magnitudes of the ion radii were taken from other papers, [10], [11] and [14].

b) The quantities of copper introduced into the luminophores were too small (maximum 0.1%) for the changes in the lattice constants to be measured.

c) It is possible that the comparatively larger quantities of the fluxing agent NaCl made it possible to measure the changes in the lattice constants, but we were not, however, able to observe this since no one luminophore was produced without the fluxing agent.

The results of our investigations are in agreement with those given in literature. Bağ et al. [12] made röntgenographic studies of changes in lattice constants of the luminophores ZnS-Cu-Pb with NaCl as fluxing agent in amounts of 2%. It was found that this fluxing agent noticeably increased the lattice constants of the ZnS unit cell. The incorporation of $2.3 \cdot 10^{-1}$ lead into the crystalline lattice of the luminophores ZnS-Pb causes a reduction of the unit cell along the a axis. The changes in lattice constants due to the introduction of copper in amounts of $9.2 \cdot 10^{-4}\%$ into the luminophore are within the limits of error in measurement.

Kolm et al. [13] carried out röntgenographic studies of constant changes in the lattice constants of GaAs into which elements of the 4-th group of the periodic table were incorporated in amounts of 0.5% to 5%. Though the ion radii of, for example, Sn and Pb are much greater than those of the basic substance ions (Ga — 1.26 Å; As — 1.18 Å; Sn — 1.40 Å; and Pb — 1.46 Å) instead of an increase in the lattice constants they found a decrease.

TABLE III

The amount of both phases in particular luminophors

No of the sample	The amount of wurtzite	The amount of sphalerite	Remarks
1	much	little	Broadening of interference lines, high-angular doublets indistinct.
2	much	much	
3	much	much	Lines sharp, doublets distinct.
4	much	much	
5	much	much	
6	much	very much	
7	much	much	
8	much	much	

According to the most recent papers [15], the authors of paper [13] were probably in error because they took too great a value for the lattice constant of pure GaAs instead of (5.6559 Å).

Black and Lublin [14] studied changes in the lattice constants of the GaAs unit cell to which Zn and Cd was added. They employed a röntgenographic method of high precision ± 0.0002 Å. Zinc and cadmium of ion radii of 1.31 Å and 1.48 Å were incorporated into the lattice in place of Ga ions (1.26 Å). Contrary to expectation, they did not cause an increase in lattice constants.

As was suggested in the introduction to the present article, in all the luminophores investigated röntgenographically two phases, wurtzite and sphalerite were observed. The quantitative relations of both phases in the various luminophores are presented in Table III. As can be seen from this table, luminophore I-1 (sample 1) with a small

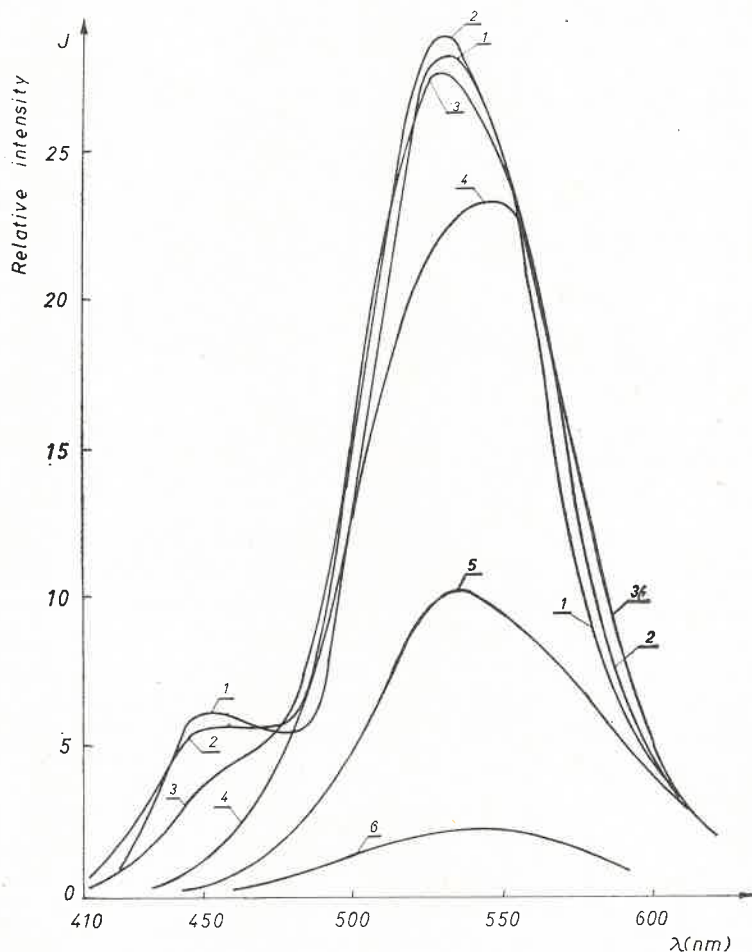


Fig. 1. Luminophor I-1 - 1% NaCl; Cu - $4 \cdot 10^{-5}$. Spectral distribution of intensity at various temperatures: 1 - 100 K, 2 - 200 K, 3 - 300 K, 4 - 400 K, 5 - 500 K, 6 - 600 K

activator and fluxing agent content is particularly exceptional. Its interference lines on the röntgenogram are broadened and the its high-angular doublets lack sharpness. Probably, a higher fluxing agent content in the luminophore gives sharp interference lines and distinct doublets, since such is the case as regards to all the other luminophore samples

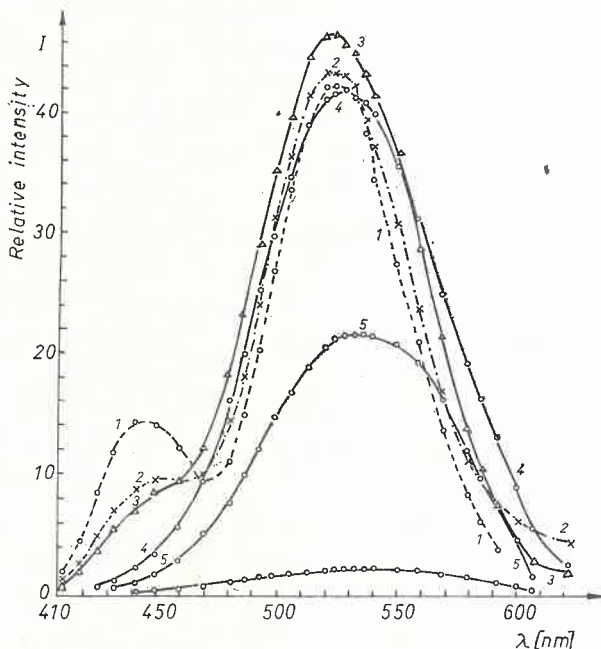


Fig. 2. Luminophor I-5 - 5% NaCl; $\text{Cu} - 4 \cdot 10^{-5}$. Spectral distribution of intensity at various temperatures: 1 - 100 K, 2 - 200 K, 3 - 300 K, 4 - 400 K, 5 - 500 K, 6 - 600 K

examined röntgenographically. In addition, in agreement with [4], luminophores I-1 excited by a wave-length of 365 nm give a green luminescence band of a comparatively low intensity. This is illustrated by the comparison of the photoluminescence intensities of the luminophores, I-1 and I-5 (samples 1 and 2), presented in Figs 1 and 2. Both luminophores discussed here were produced under identical technological conditions excited by radiation of the same intensity and the measurements were made under the same geometrical and electronic conditions, the only difference being that the amount of fluxing agent introduced into luminophore I-5 was five times greater. As the figures show, the intensity of the band of lum. I-5 are considerably greater than those of the corresponding band of lum. I-1 measured in same relative units. This was probably due to the fact that too small an amount of fluxing agent NaCl was introduced into lum. I-1, the chlorine of which comprises the donor level. It would therefore seem that one of the levels responsible for the radiation transition related to the green band is the chlorine donor level. The other level may be the copper acceptor level. According to the Apple-Williams model [16] both these levels are associated with each other.

The photoluminescent properties of sample 3 (lum. I-8) differ from those of lum. I-5 only in that the intensity of the bands is considerably lower. This is evident in Fig. 7 of [4]. As Table III shows, in sample 1, the wurtzite phase predominates whereas the next two have equal wurtzite and sphalerite phases. It would therefore seem that the increasing concentration of the fluxing agent NaCl in the Group I luminophores causes a gradual change of the wurtzite phase into the sphalerite phase.

From Group II, 5 luminophores of a copper concentration varying from zero to 10^{-3} g per 1 g ZnS were examined röntgenographically. From Table III it would seem samples 4, 5, 7, and 8 have a large wurtzite phase content and a large sphalerite. This is due to the large quantity of fluxing agent NaCl introduced — 4%. Sample 6 (lum. II-5), on the other hand, contains little of the wurtzite phase and a large sphalerite phase. The reason for this was the addition of a high concentration of copper 10^{-3} g per 1 g ZnS.

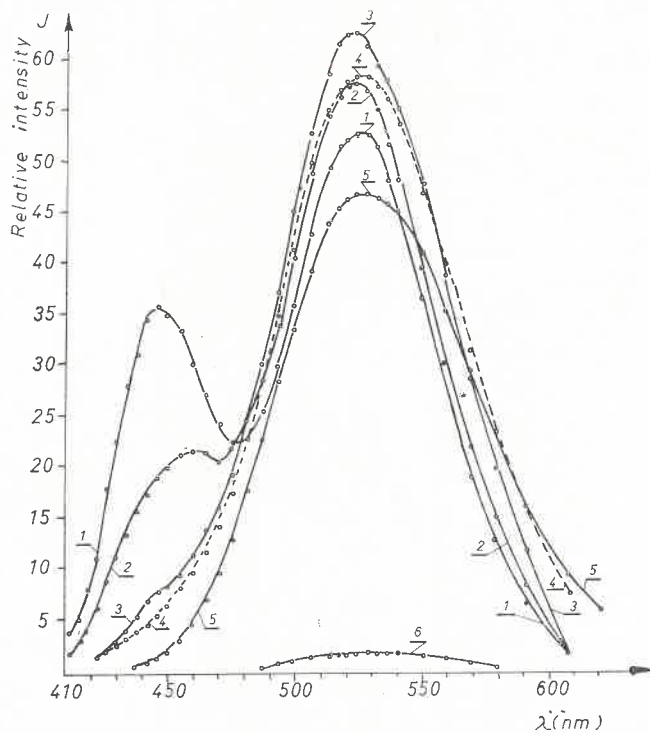


Fig. 3. Luminophor II-6; Cu — $2 \cdot 10^{-4}$; NaCl — 4%. Spectral distribution of intensity at various temperature: 1 — 116 K, 2 — 198 K, 3 — 293 K, 4 — 347 K, 5 — 426 K, 6 — 520 K.

It is also seen from Table III that the increasing concentrations of both types of admixture, both the activator and coactivator, cause a change from the wurtzite phase to the sphalerite. No other structural peculiarities in Group II were found.

However, as regards to photoluminescent properties, the group of luminophores investigated was found to be far more varied than Group I, thus lum. II-0 (sample 4), without the activator, gives a blue band of self-activated ZnS of a comparatively low

intensity. Luminophores with a copper concentration of from 10^{-5} to 10^{-4} g per 1 g ZnS (e. g. sample 5) give a green band of high intensity quite similar to that shown in Fig. 2. It is worth noting that a tenfold change in activator concentration affects only the intensity of the luminescence of these luminophores, increasing it, but does not change the character of emission. A higher concentration of copper only increases the intensity of the blue band at the cost of a decrease in that of the green band.

A further variety in the photoluminescence properties is observed in lum. II-6 and II-6a (sample 7 and 8). They contain an equal concentration of activator but differently incorporated. Lum. II-6 was produced by the usual method of sintering the basic substance,

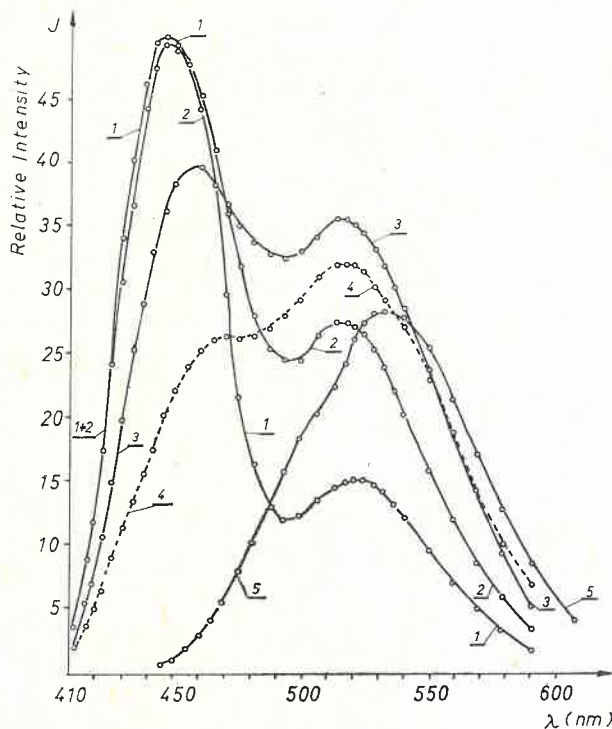


Fig. 4. Luminophor II-6a; 10^{-4} Cu + 4% NaCl + 10^{-4} Cu introduced with diffusion method. Spectral distribution of intensity at various temperature: 1 - 116 K, 2 - 198 K, 3 - 293 K, 4 - 347 K, 5 - 426 K

activator and fluxing agent. On the other hand, lum. II-6a was obtained from lum. II-3 (sample 5) by diffusive incorporation of additional amounts of copper, 10^{-4} g per 1 g ZnS, at a temperature of 450°C for 30 minutes. Their luminescence spectra differ greatly. This is seen in Figs 3 and 4 where great differences in the intensity of both the blue and green copper bands occur particularly at low temperatures. As was shown in previous papers [1] and [2], the copper diffusively incorporated in lum. II-6a in the present investigations changed the green luminescence centres into blue centres, but because of its small ionic radius it did not bring about any noticeable change in the structure of the luminophore.

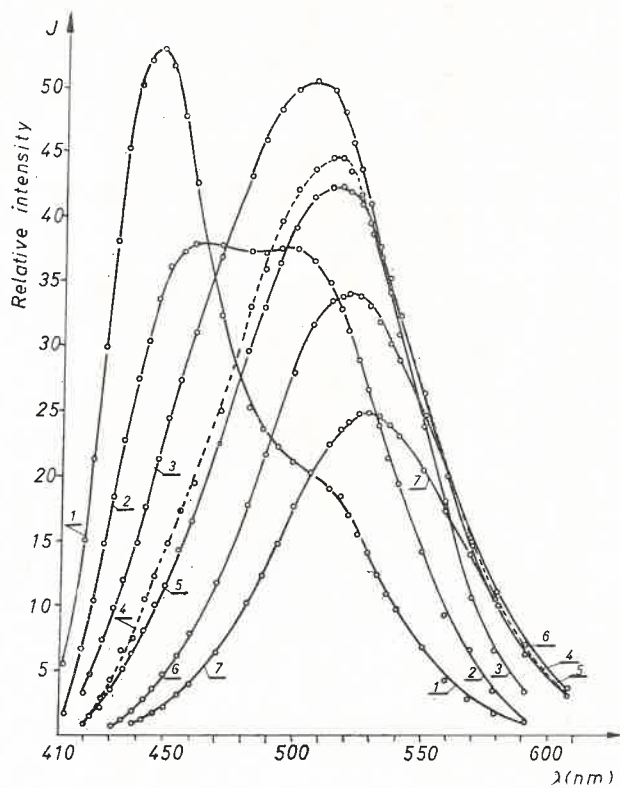


Fig. 5. Luminophor II-4; $\text{Cu} - 5 \cdot 10^{-4}$, $\text{NaCl} - 4\%$. Spectral distribution of intensity at various temperature: 1 - 116 K, 2 - 198 K, 3 - 293 K, 4 - 347 K, 5 - 426 K, 6 - 520 K, 7 - 600 K

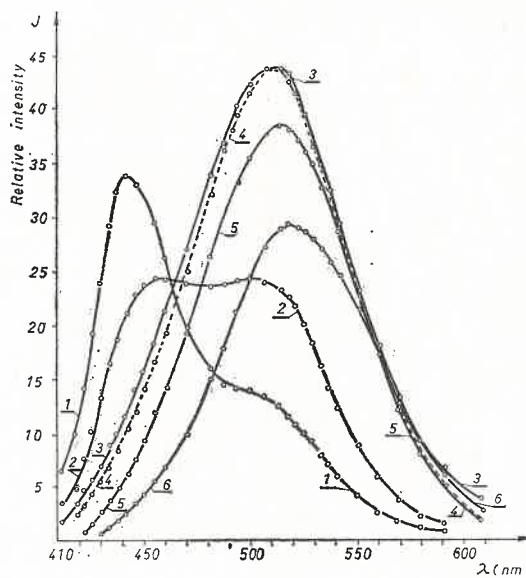


Fig. 6. Luminophor II-5; $\text{Cu} - 10^{-3}$, $\text{NaCl} - 4\%$. Spectral distribution of intensity at various temperature: 1 - 116 K, 2 - 198 K, 3 - 293 K, 4 - 347 K, 5 - 426 K, 6 - 520 K

In our previous papers it was found that the blue luminescence centres of copper can also be obtained in luminophores prepared by the usual method requiring only the addition of a higher concentration of the activator than usual. In Figs 5 and 6 the luminescence of luminophores II-4 and II-6 (sample 6) with a copper concentration of $5 \cdot 10^{-4}$ and 10^{-3} g per 1 g ZnS are shown. As can be seen from these figures at the lowest temperature of the tests (116 K) the blue copper band reaches a high magnitude, whereas at a temperature of about 200 K the intensity of the bands is equal. This corresponds to the equilibrium of both types of luminescence centres. Moreover a two-fold increase in the copper concentration in lum. II-5 as compared with lum. II-4, does not change the character of emission but merely results in an considerable extinction of concentration.

A comparison of the appropriate curves in Figs 4 and 5 shows that the blue luminescence centres obtained by the diffusion method of incorporating copper in the luminophore are more stable. This means that in the method the equilibrium of blue and green copper centres is displaced towards higher temperatures by over 100 degrees (curve 2, Fig. 4 and curves 3 and 4, Fig. 5).

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