

# Detection of structural varieties of red gem spinels from Ratnapura, Sabaragamuwa province of Sri Lanka

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A new instrumental method for spectrographical detection of particularities of crystal fields around optically active ions, such as the trivalent chromium ion, was applied to an investigation of red magnesium-spinels from the Ratnapura gem gravels; also from Kangaiyam in India and some other sources for comparison.

The method is characterized by analysis of luminescence spectra in the red and near infrared ranges excited by a concentrated flux of blue radiation, and analysed with a spectrograph of considerable optical power. Spectrograms are enregistered on photographic material of high resolving power; they reveal multiplet structures and intensity-distributions of component lines. Slight variations in spectral structure are significant for the detection of structural varieties of minerals.

Systematic investigation of the spinels revealed the existence of a hitherto unknown variety of red gem spinel, provisionally named spineloid. Its properties are described.

Numerical data on the resolved luminescence spectra, in the wavelength range between 6500 Å and 7600 Å, are given for the normal and extraordinary varieties. Other physical properties of both varieties are reviewed and compared.

The results of the investigation are discussed, and evaluation of data leads to a tentative conclusion regarding the nature of the spineloid structure. The spineloid is a stoichiometric or near stoichiometric spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) in which  $\text{Cr}^{3+}$  ions appear in pairs in regular polyhedral configurations; the spectrum is modified by the presence of manganese ions of different valencies.

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Introduction	2
Research methods	4
General principles	4
Instrumental methods	5
Materials investigated	7
Material from Sri Lanka	7
Material from India and from other sources	9
Spectrographic investigation of the luminescence of spinel varieties	11
Materials selected	11
Method of examination	11
Parameters determined	13
Results of the measurements	13
Preliminary conclusions	15
Evaluation of results, discussion and conclusion	18
Comparison of common physical properties of the normal red spinel and of the spineloid	18
Synthesis of the characteristics of the spineloid	19
Comparison of properties	20
Discussion and conclusion	24
Summary	25
References	27

## Introduction

Up to the present, spectroscopy found only restricted application in mineralogy. The technique is mainly used for rapid detection of certain important minerals, and very seldom for the detection of mineral varieties (see for example Zwaan, 1957). From the point of view of solid state physics too, few attempts have been made to interpret mineral spectra. Still, such spectra can yield detailed information about the active ions which cause them and about the surrounding crystal field.

In the course of his studies on the optical properties of crystals, the author succeeded in developing an instrumental method, which makes it, as a normal practice, possible to obtain more detailed and precise information on absorption and luminescence spectra. The principles of this method are described in the author's thesis (Lagerwey, 1973). With the aid of this method, a relatively large number of minerals – including gemstones – were examined; this led to the discovery of a new variety of scheelite, among others.

In principle, use is made of a method of excitation of luminescence, which

in many cases has prominent advantages over conventional methods: luminescence is excited by a concentrated flux of radiation in the blue range of the visible spectrum, instead of a low density flux of ultraviolet light. This blue radiation does not cause changes in the crystals examined (for instance changes in colour); this is a great advantage in the testing of gems. For the generation of spectra, use is made of a refined type of multi-prism spectrograph. Characteristic for this instrument are: a sufficient aperture of the optical elements, resulting in a good luminosity of the spectra; a high resolving power, which allows a good separation of closely spaced spectral lines, and finally registration of the spectra on photographic materials with a correspondingly high resolution.

In this manner, spectra are obtained, which show fine-structures of line groups. From these, information can be obtained about the energy levels and transitions in the optically active ions in a particular crystal field.

One of the best ions for structure-tracing is the trivalent chromium ion. This ion is present in a great number of current minerals, and causes prominent absorption and (sometimes) luminescence line spectra. In the ion, energy changes take place in the outer electron shell but one, the outer shell being completely filled. Thus, the outer shell functions as a shield of moderate effectivity for external electrical fields, such as a crystal field. This means that the energy changes in the chromium ion are modified in a limited degree: its main characteristics remain apparent in the spectra and the effects of the surrounding crystal field are clearly recognizable. As examples we mention the spectra of ruby, spinel, alexandrite, pyrope garnet, topaz from Ouro Preto, etc.

One of the objects of the author's studies is to show that by further development of his instrumental method finely structured spectra can be obtained. By measuring and interpreting these, conclusive data can be gained about the structure of varieties of minerals.

The range of minerals represented in the gem gravels of Sri Lanka (formerly Ceylon), many of which have a chromium content, forms an ideal object for such an investigation. Spectroscopic survey of several batches of stones from Ratnapura (Sabaragamuwa province), taken from the author's collection (numbers prefixed with an S) and from the one of the Rijksmuseum van Geologie en Mineralogie (numbers prefixed with RGM), showed that red spinel is one of the most attractive objects for spectrographic research. The chromium spectrum of spinel differs rather strongly from the chromium spectra of the other minerals mentioned and luminescence of the spinel is often intense. For this reason, these red gem spinels were chosen for the present research. During the survey a new variety of spinel was discovered.

In the present article, the results of research on the common and the extraordinary variety of spinel are given together with extensive numerical data on the fine-structure of the spinel spectra in the red and near infrared ranges of the spectrum.

#### *Acknowledgements*

The author wishes to thank the direction and the staff of the Rijksmuseum van Geologie en Mineralogie (the Netherlands National Museum of Geology and Mineralogy) – and Dr P. C. Zwaan in particular – for their active co-operation and

for making available important mineral samples. He is also much indebted to Mr A. G. Bode, of the Hague, who – in the interest of gem research – did not hesitate to lend some unique gemstones from his collection; and to Professor Dr P. Hartman of the Institute of Geology and Mineralogy of the University of Leiden for his assistance in making x-ray diffraction analyses.

## Research methods

The methods, used in the present investigation, are unconventional. For this reason, it appears necessary to explain them in some detail, without marring the descriptive and demonstrative character of the article by a mass of theoretical considerations.

### GENERAL PRINCIPLES

A review of the main principles has already been given in the introduction, and we will restrict ourselves to a discussion of further essentials (see also Pohl, 1967). In the present research, ions of elements, in which energy changes are taking place in inner electron shells, are used as indicators of the nature of the surrounding crystal field. The trivalent chromium ion is a most efficient tracer ion because of its single shielding. In this ion, energy changes are taking place in the N-shell electrons. These can assume a number of energy states, which are characteristic. If an electron absorbs a certain quantity of energy (a quantum of a certain wavelength), its energy is raised to a higher level: characteristic absorption. When the electron returns to its original energy state, the energy absorbed may be radiated on the same wavelength: characteristic luminescence. In principle, the ion possesses a number of discrete energy levels with an associated number of possible energy changes between a pair of levels and a corresponding number of characteristic wavelengths of absorption and luminescence. The result is a structured line spectrum.

A second parameter of the line spectrum is the intensity of the lines. The greater the number of quanta absorbed or radiated, the greater will be the intensity of a line. The number of quanta for each transition is governed by its probability. Thus, the (relative) intensity of a line is a direct function of the probability of an energy change, which is also characteristic for the ion and its state.

Now, the energy states in a partly shielded ion are influenced by the configuration of surrounding electrical fields. Such a configuration is found in a crystal lattice, where the electrical field is a consequence of the matrix structure. Thus, the energy scheme of the active ion is not only a function of the nature of this ion, but also a function of the surrounding crystal field. Therefore, the line spectrum is characteristic for both the active ion and the crystal lattice, showing lines of specific wavelengths and intensities.

The instrumental method, developed for the purpose, makes it possible to obtain a highly resolved spectrum showing groups of fine lines and registering

their intensities. Such a spectrogram is a transformed image of the energy changes, and their probabilities, of the active ion in its specific matrix. It is a true fingerprint of the mineral variety in question.

Absorption spectra are different from luminescence spectra. When specific absorption takes place, an inner electron of the chromium ion, for example, is raised to a higher energy level. Later, this energy may be dissipated as heat or be transferred to another type of ion, as the electron returns to its original state. In this case, there is no specific radiation from the original active ion. In the spectrum we see a dark line of corresponding wavelength. However, energy changes between the ground state of the electron and one or more levels of higher energy may be reversible; there is absorption and luminescence possible on one and the same wavelength. These reversible lines or resonance lines are typical for the chromium ion; usually they appear in groups of two, called *doublets*. Notable examples are ruby, topaz from Ouro Preto (heat treated), emerald and alexandrite.

Other minerals, like chromediopside and pyrope, show this doublet, but only in the absorption spectrum: luminescence is absent, because the energy released by the chromium ion is transferred to other ions, and converted without radiation to heat.

The spinel, containing the trivalent chromium ion, forms a class apart: its spectrum is of a more complicated nature, and it does not show the doublet, prominent in the other minerals. The spectrum consists of a number of luminescence bands, which can be dissolved in a group of closely spaced lines called multiplet. This spectrum is highly characteristic and it is a very sensitive indicator of particularities in the spinel lattice. Fig. 1 shows such a resolved spectrogram of trivalent chromium in the normal  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel lattice. The properties of this

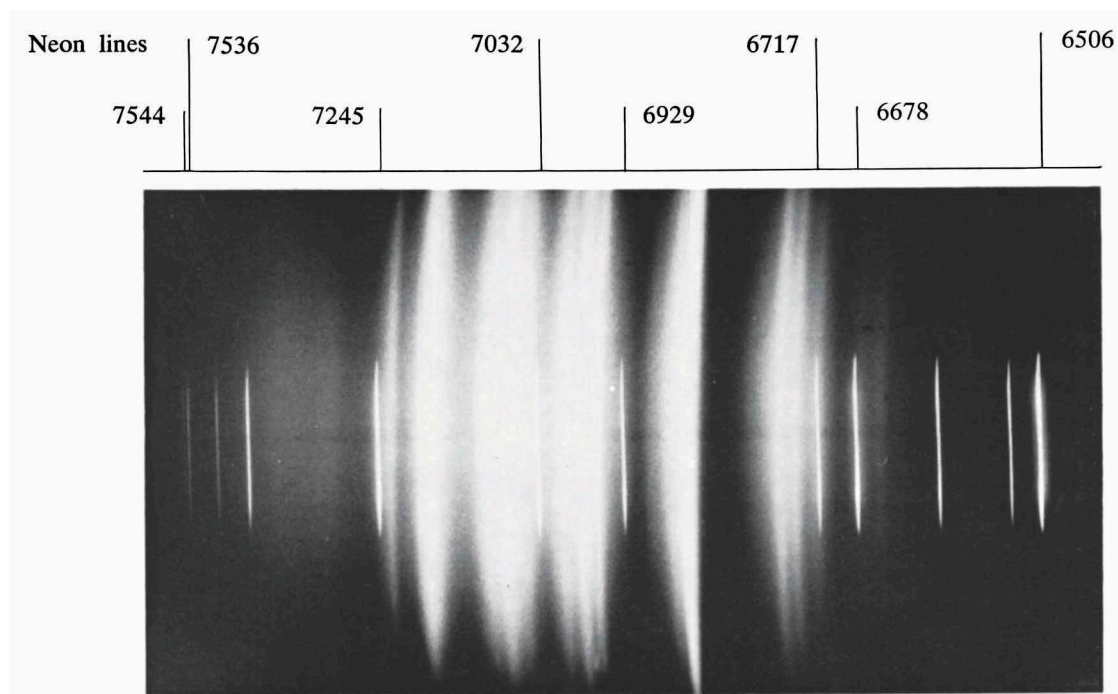


Fig. 1. Resolved multiplet structures in the luminescence spectrum of the trivalent chromium ion in common red spinel from Ratnapura, Sri Lanka (S 64). Wavelengths in Ångström Units.

variety of spinel are constant and even in the spectra of these spinels from *various* mineral deposits only minor differences can be found.

During the examination of a large number of spinel grains, however, a stone was discovered with an abnormal luminescence spectrum in the near infrared range. Here, the *wavelengths* of radiation of the  $\text{Cr}^{3+}$  ions are practically the same as those of the common red spinel, but the *intensities* of the spectral lines are differently distributed (second order effect). This seems to indicate, that the crystal lattice of the extraordinary stone is a modification of the normal spinel lattice.

This discovery confirms the practicability of the method for the detection of mineral varieties, distinguished by modifications of the lattice structure.

#### INSTRUMENTAL METHODS

In this section, only methods applied to the research of the chromium spectra of spinels in the red and near infrared ranges will be discussed. The three most important features are: the method of excitation of luminescence, the characteristics of the spectrograph used, and the photographic material for registration.

The red luminescence of the trivalent chromium ion in the spinel is most effectively excited by a wide-band radiation in the wavelength range between 5800 and 4000 Å, as is shown by examination of the excitation spectrum. In this range, the spectrum is continuous with maximum energy at the long-wave end of the range. A useful source for this radiation is a halogen-cycle incandescent lamp with a filament of the smallest possible surface; for instance low voltage projection lamps of 250 Watts or 400 Watts. The light of this lamp is concentrated in a parallel beam in which a watercooled cell, provided with planparallel windows and filled with a saturated solution of coppersulphate, is located. Near the object, the beam is focussed by means of a condensor lens. In this manner, very high energy densities can be reached. The intensity of the luminescence is correspondingly high. The optical axis of the exciting beam cuts the optical axis of the spectrograph at an angle of 45° (see also Lagerwey, 1973).

The light, re-emitted by the crystal, is concentrated by an achromatic lens system on the entry slit of a spectrograph; a filter with a cut-off wavelength of 6000 Å removes the exciting light component.

The spectrograph separates the light to be analyzed in measure of its wavelength. The instrument is characterized by its dispersive power, by its resolving power, and by its aperture.

The length of the projected spectrum, measured between certain wavelengths, is a measure of the dispersive power. This power can then be expressed in terms of Å per mm length of spectrum. In our case, a multi-prism spectrograph with a dispersion of 30 Å per mm at a wavelength of 7000 Å was used.

A most important characteristic of the spectrograph is its resolving power, that is the capacity to separate closely situated spectral lines. As a measure, the quotient of the average (medial) wavelength of two lines, and the difference in wavelength, both in the same units, is used. Thus, for the separation of the sodium D lines, the required power of resolution is  $589.294 : 0.597 = 987$ . In our case, for clear separation of multiplet component lines, the spectrograph should have a resolving power of more than 30 000.

The aperture of the instrument determines the intensity of the spectrum. The ratio between the focal length and the diameter of the collimator lens serves as a measure; it should not exceed 10. The glass optical elements, used in the spectrograph, are suitable for a wavelength range of 3800 to 10 000 Å. It is possible to register spectra in the near infrared range, which is very important.

For the registration of the spinel luminescence spectra, infrared sensitive material must be used as the lines of maximum intensity lie in the range between 6800 Å and 8000 Å. This photographic emulsion should also have a good sensitivity in the visible red range down to about 6000 Å. The resolving power of the emulsion must be of at least the same order as the one of the spectrograph. If the conditions, mentioned above, are satisfied, spectrograms, suitable for structural analysis can be obtained.

## Materials investigated

In the preceding part we have stated — anticipating research results — that the luminescence spectra of red spinel crystals of the common variety are identical, for all practical purposes: they are characteristic for the crystal lattice of  $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cr}^{3+}$ . We also mentioned the detection of a spinel variety, possessing an extraordinary chromium spectrum (second order variation). These statements are based on spectroscopic examination of a large number of stones from different sources.

In this section, we will describe the materials investigated and — in the case of the pebbles from Ratnapura — some selection methods. Red gem spinel is a rather rare material. Good material could only be obtained from Sri Lanka and from India, apart from some large cut stones of remarkable beauty — of unknown origin — which Mr A. G. Bode of The Hague kindly put at the author's disposition.

### MATERIAL FROM SRI LANKA

The following basic material of known origin was examined:

About 300 g of mixed pebbles, all of them smaller than 4 mm in diameter, from the Ratnapura gem gravel pits in the Sabaragamuwa province.

A quantity of mixed pebbles from the same source, weighing about 5 g, which Mr Bode recently presented to the author.

Some mixed spinels from a batch (RGM 81 723) of the Museum's stock; from this batch a mauve coloured spinel pebble (RGM 163 329) was selected. All stones are from Ratnapura.

A cut spinel of 1.35 carats of a light, spinel-red colour, RGM 150 888 bought in Sri Lanka.

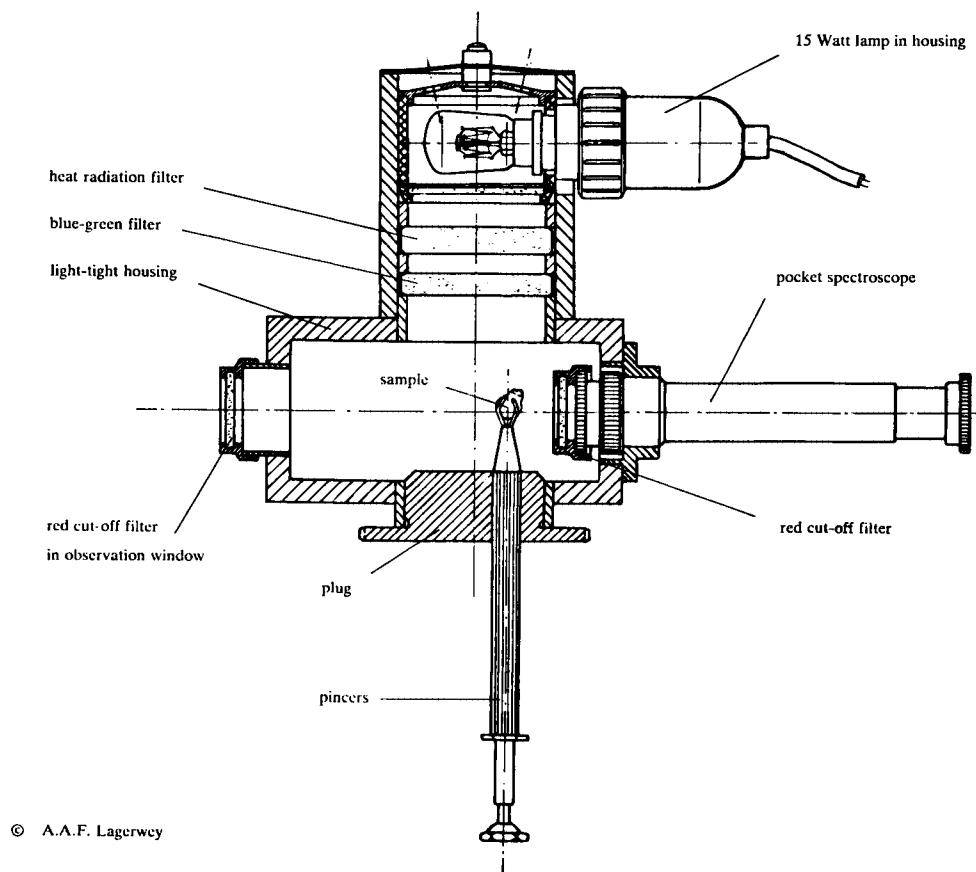
About the last two items nothing special is to be mentioned, for the present.

From the first two batches of mixed pebbles, spinels had to be selected. In the case of the author's material, this separation was carried out, some time ago, in the following way:

Firstly, the whole quantity was separated in fractions of different densities by means of the sink-and-float method, using a progressively hydrated mixture of thalliumformate and thalliummalonate (Clerici's solution). Rubies were separated in the density range between 3.90 and 4.00, and spinels in the range between 3.50 and 3.80. The weight of the spinel fraction was about 160 g, from which 100 g showed a good luminescence (about a thousand grains).

Next, these pebbles were examined spectroscopically. For this selection, a simple apparatus — a diagram of which is shown in fig. 2 — was used. Each stone, gripped in jewellers pincers, was inserted in a fixed position in the black walled chamber, flooded with blue, filtered, light from a 15 Watt lamp. The light emitted by the stone could be analyzed with a pocket spectroscope, fixed in the side wall of the chamber, with a red cut-off filter clamped before the slit. As the spectrum of the normal red spinel is very conspicuous, the spinels could be checked without trouble. Its main luminescence line at 6857 Å lies in between those of ruby (doublet around 6935 Å) and alexandrite (doublet around 6795 Å).

From the batch of spinels, a number were put aside for spectrographical analysis. Their spectra, checked with a spectrometer of larger dispersion, were identical. In the same spinel fraction of 160 g, as previously mentioned, *one* pebble was found, which had an abnormal luminescence spectrum, its main line at 6886



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Fig. 2. Apparatus for spectroscopical selection of mineral grains.



A lying between those of ruby and spinel. This spectrum was found to be different from the spectra of all known chromium containing minerals, and therefore the stone was kept for detailed investigation: it bears the series number S 99 (see the next chapter).

The pebbles given by Mr Bode to the author were sorted spectroscopically; about two grams of red spinels of a light colour were separated. Spectrometric investigation proved all thirty stones to be of the normal variety.

#### MATERIAL FROM INDIA AND FROM OTHER SOURCES

Apart from the Ratnapura spinels, the author disposes of two perfect octahedral crystals of red gem spinel from Kangaiyam, in the Selam district (Madras province, Republic of India). These crystals are registered under S 111 of the author's collection; they weigh 0.48 carats (0.096 g) and 0.43 carats (0.086 g). Their colour is a rather dark red with a slight purplish tinge (R.H.S. Colour Chart 57A - 58B). Earlier, extensive, spectrometric investigations showed that these spinels have the normal luminescence spectrum in the *red* range. In spite of the intense red colour, it was impossible to observe the absorption lines of trivalent chromium (reversal of luminescence lines). The intensity of the luminescence is much lower than the same of the Ratnapura spinels.

In order to obtain further data and — if possible — to make observations on the reversal of spectral lines, Mr Bode kindly put several large spinels from his collection at the author's disposal for examination. These magnificent stones, all of unknown origin, can be described as follows:

Bode A — A light coloured spinel of a typical spinel-red colour, emerald cut (R.H.S. Colour Chart 55C). It weighs 5.80 carats (1.1615 g). According to determinations made by Dr Zwaan, the refractive index is 1.715 (a normal value, see also Webster, 1962, pp. 101, 102) and the density is 3.579.

Bode B — A deeper coloured spinel, also of a typical spinel-red colour (R.H.S. Colour Chart 55A); emerald cut. Its weight is 4.31 carats (0.8626 g). The refractive index is 1.716 and the density is 3.592 (Dr Zwaan).

Bode C — A purplish-red spinel (R.H.S. Colour Chart 75A) of mixed cut, and a weight of 2.81 carats (0.5624 g). The refractive index is 1.717 and the density 3.587 (Dr Zwaan).

The refractive indices were measured on the table facets of the stones with the aid of a Rayner diamond refractometer. The densities were determined with the aid of a hydrostatic balance; 1,2 dibromoethane was used as immersion liquid.

The spinels A and B show an extremely intense red luminescence, when excited by blue radiation; the luminescence of the purplish spinel C is much weaker. Spectrometric investigation showed that all three spinels were of the normal spectral type.

In the author's opinion, considering their colour gamma, it seems probable that the stones are from Sri Lanka; it is a great pity that no stones originating from Burma were available for comparison.

The luminescence-spectra of the stones Bode A-C are shown in figures 3-5 together with a calibration-spectrum of neon. The wavelength range is between 6500 Å and 7600 Å.

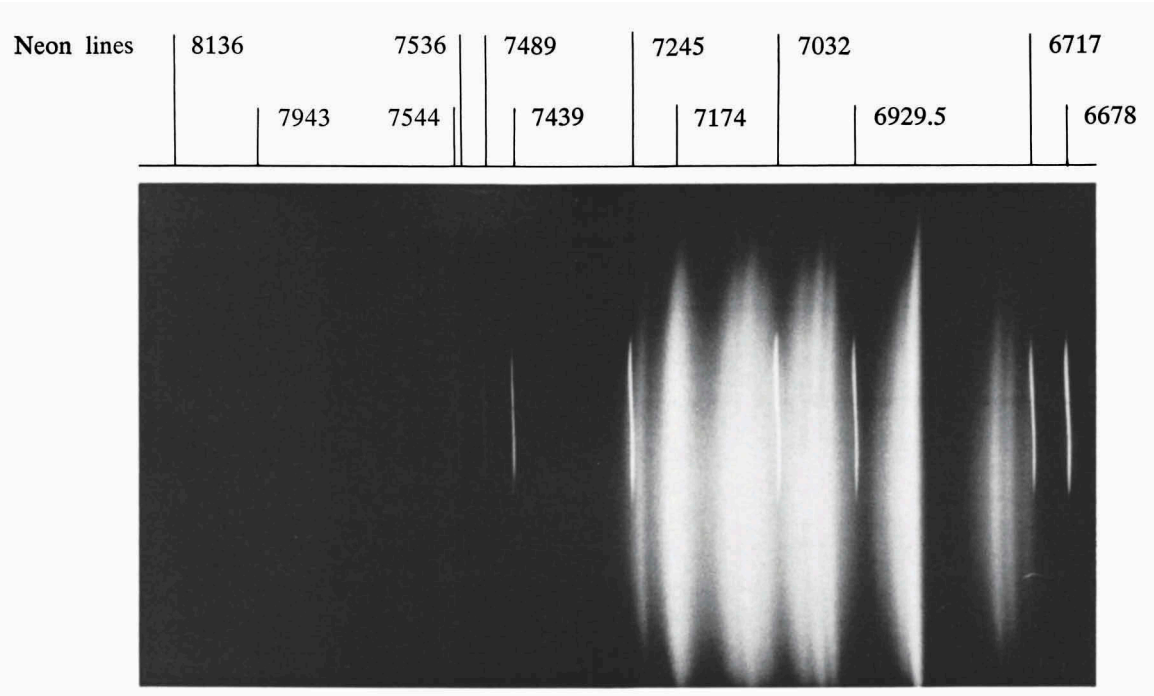


Fig. 3. Resolved luminescence spectrum of red gem spinel (Bode A) in the near infrared region. Wavelengths in Ångström Units.

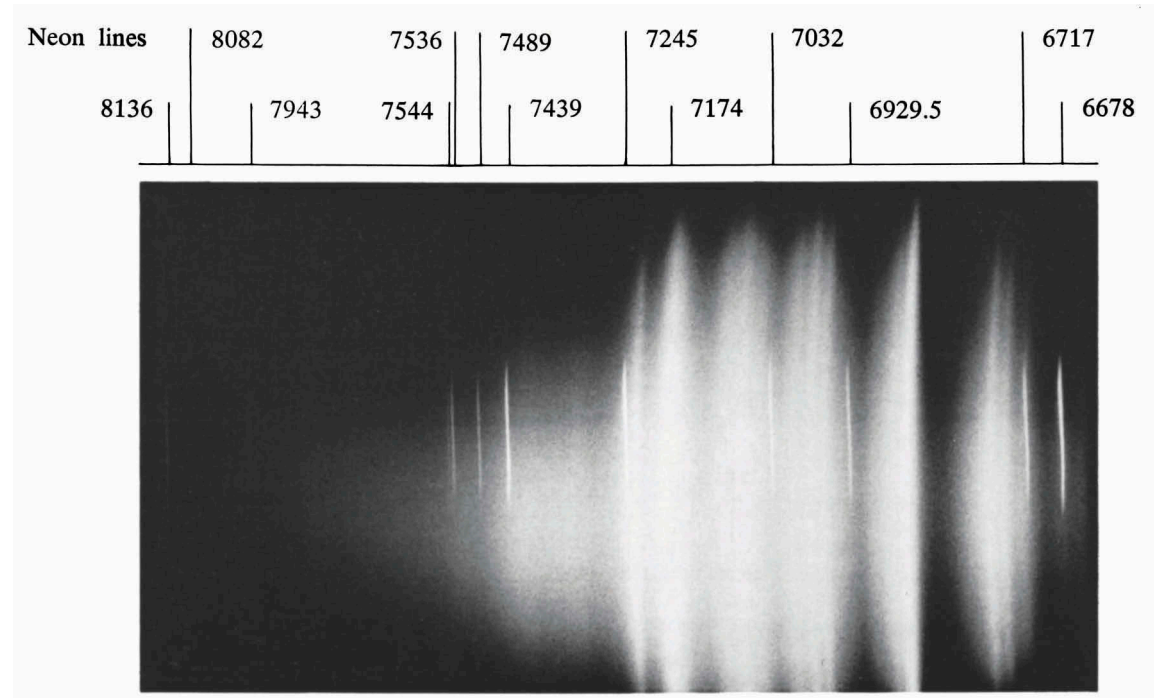


Fig. 4. Resolved luminescence spectrum of red gem spinel (Bode B) in the near infrared region. Wavelengths in Ångström Units.

## Spectrographic investigation of the luminescence of spinel varieties

The purpose of this investigation was to obtain precise data, employing excitation of luminescence with blue radiation in combination with the use of a spectrograph of considerable dispersive power, of the spectra of the  $\text{Cr}^{3+}$  ion in red spinels of the normal variety, and in the extraordinary variety. On the basis of these data, a distinction between the two varieties is made.

### MATERIALS SELECTED

The luminescence of the following materials was spectrographically analysed in the wavelength range between 7600 and 6500 Å:

A light pink coloured monocrystalline fragment of spinel from Ratnapura (S 64, see p. 7 to 9, spectrogram fig. 1) selected from the 300 g batch.

A mauve coloured monocrystalline fragment of spinel in the shape of a flat, water-worn pebble; also from Ratnapura (RGM 163 329, see p. 7).

A cut spinel (RGM 150 888, see p. 7, spectrogram fig. 6).

A red octahedral crystal of 0.48 carats from Kangaiyam (S 111, see p. 9).

The three cut spinels (Bode A-C) on exposition in the Museum (see p. 9, and the spectrograms figs. 3-5).

All these spinels were proved to be of the normal type, and their spectra in the wavelength-range studied (6500 Å to 7600 Å) are identical in the first and second order.

A purplish monocrystalline fragment of the extraordinary spinel type from Ratnapura; it shows an anomalous luminescence spectrum (S 99, see p. 8, spectrogram fig. 7).

### METHOD OF EXAMINATION

The luminescence of the crystals examined was excited with blue radiation in the wavelength-range between roughly 4000 Å and 5800 Å, obtained by filtering from the continuous radiation of a high power halogen-cycle incandescent lamp. The flux of blue light was focussed on the crystals by means of a system of lenses. The light, re-emitted by the crystal, passed a red low frequency pass filter with a cut-off wavelength of 6000 Å to remove the exciting radiation component; it was concentrated on the entry-slit of a multiple prism spectrograph by an achromatic lens. The spectrograph used had a dispersion of 30 Å per mm at a wavelength of 7000 Å, measured in the focal plane. The power of resolution is better than 30 000.

The spectrum was enregistered on Kodak high-speed infrared sensitive film, type 2481 (see Kodak publication P-9, p. 24d). This emulsion has also a reasonable sensitivity in the visible range.

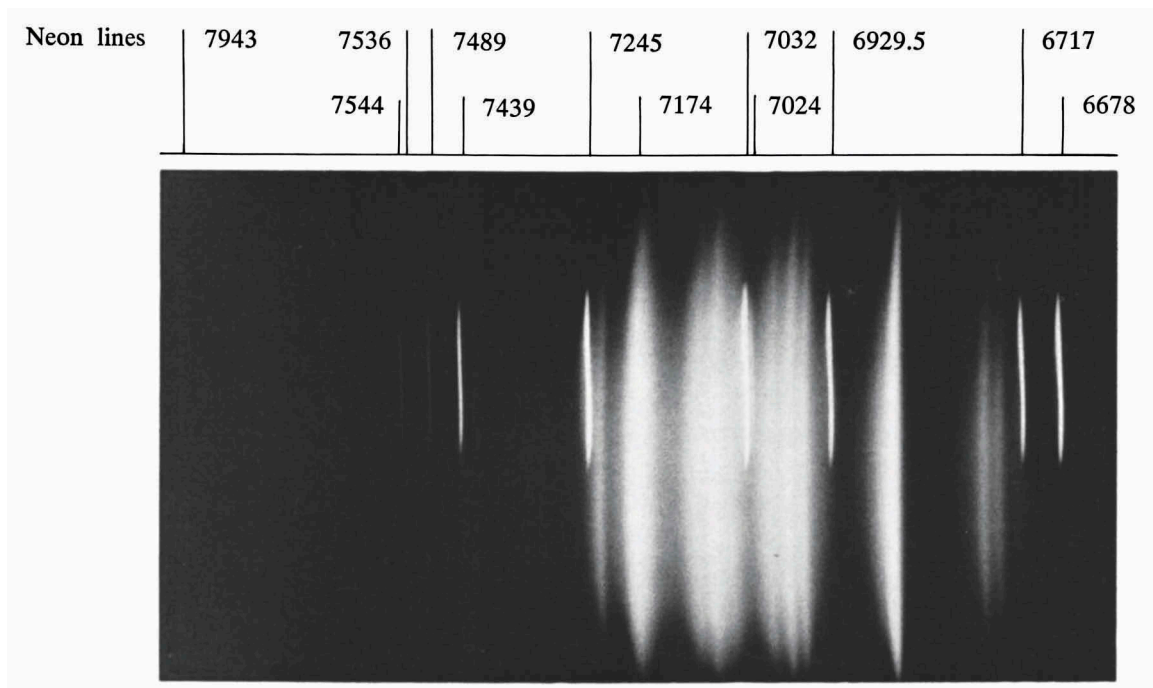


Fig. 5. Resolved luminescence spectrum of violet-red gem spinel (Bode C) in the near infrared region. Wavelengths in Ångström Units.

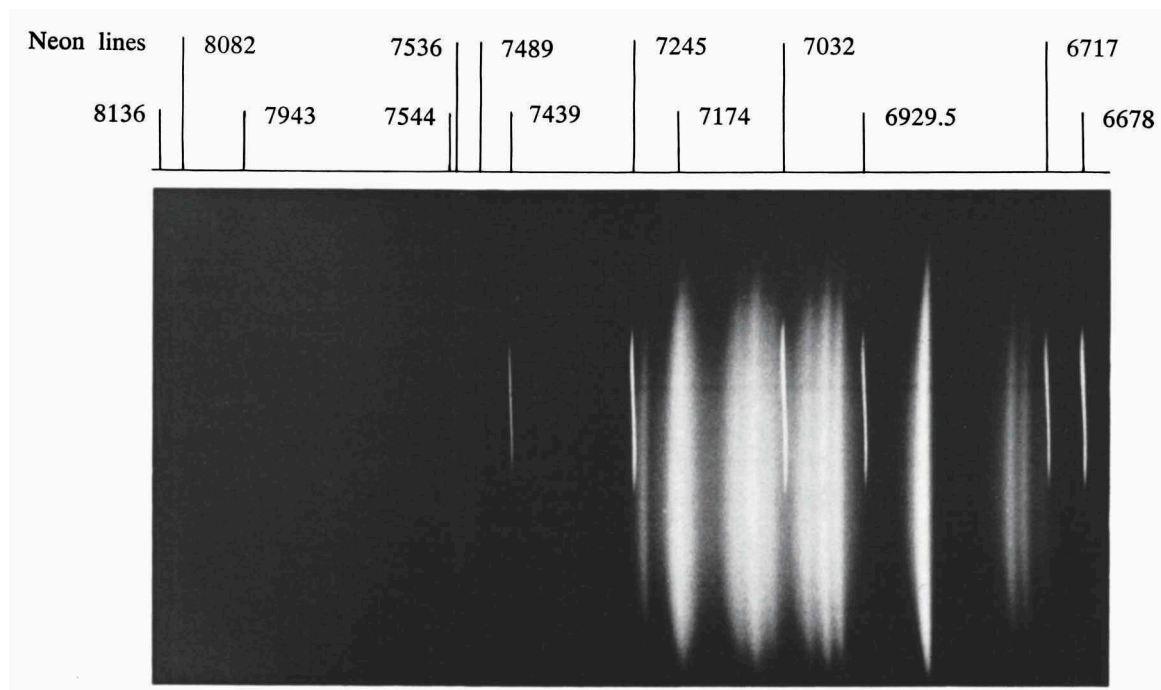


Fig. 6. Resolved luminescence spectrum of red gem spinel (RGM 150 888) in the near infrared region. Wavelengths in Ångström Units.

## PARAMETERS DETERMINED

By measurements, taken from the spectrophotograms obtained, the following parameters were determined:

The wavelength of peak intensity of each luminescence line. All wavelengths were derived of a standard spectrum of neon, which was enregistered simultaneously.

The relative intensity of the luminescence lines was determined by comparison of the densities of the photographic impressions of the lines on the Kodak film 2481. The intensity of the strongest line was set at 10. The intensities determined in this manner are obviously different from the intensities of the lines, as observed by the human eye, which becomes increasingly less sensitive for light of wavelengths exceeding 6800 Å. The film, on the contrary, is less sensitive for wavelengths lower than 6800 Å (see Kodak publication P-9, p. 24d).

The special character of each line, in particular its width, its internal intensity-distribution, and its definition.

## RESULTS OF THE MEASUREMENTS

In the wavelength-range studied, the spectrograms of all normal red spinel crystals, mentioned on p. 11, are identical up to second order effects. This can readily be seen, as the spectrograms of the figures 1 and 3 to 7 included are studied. In earlier investigations, made by the author, the same spectrum was observed. Essentially, the most intense lines seem to appear in groups of three or more (triplets or multiplets), which are almost symmetrically arranged around a central group containing the line of maximum intensity of the whole spectrum. The appearance of groups of three or more prominent lines is characteristic for the  $\text{Cr}^{3+}$  ion in the spinel lattice; in the lattices of corundum, chrysoberyl (alexandrite), emerald, and topaz from Ouro Preto, groups of two lines (doublets) are prominent.

The spectrograms of fig. 7 show the more intense lines of the common red spinel (S 64 from Ratnapura) and those of the extraordinary variety (S 99, also from Ratnapura). Superposition of both spectra makes differences and resemblances more apparent: the spectral lines of the anomalous crystal are wider and vaguer than those of the normal variety of spinel; they are arranged in similar multiple groups, but the intensity distribution of the component lines in each group is different.

The numerical results of the measurements, specified in the previous section, are arranged in Table 1 (p. 16). This table is accompanied by an elaborate explanation, to which we refer. The results, presented in the left half of the table, were obtained from analyses of the spectra of the normal red spinels, specified on p. 11. The results, presented in the right half of the table, are obtained from an analysis of the anomalous crystal fragment S 99.

The arrangement of data in the table makes it possible to correlate the spectral properties of the common variety of red spinel directly to those of the anomalous crystal. In order to make the existing relations more apparent 'at a glance', a diagram of both spectra was designed (Enclosure). Here, wavelengths of luminescence lines are indicated on a horizontal scale in the middle of the diagram,

running from 760 nm (7600 Å) on the left down to 650 nm (6500 Å) on the right. The relative intensity of each line is represented by the length of the vertical columns, measured from the central abscis-axis outwardly: the top half of the figure shows the lines of the common red spinel and the bottom half the lines of the anomalous crystal. Lines in the visible range are light red and lines in the near infrared range are shown in a darker red tone. A fringe means that a certain line is diffuse. The width of the columns is approximately proportional to the line width observed. Positions of neon-lines, used for wavelength-measurements, are also indicated. These lines are also visible as triangular peaks in the spectrograms of fig. 7, and as short lines in the central region of fig. 1 and on the other spectrograms of the same type.

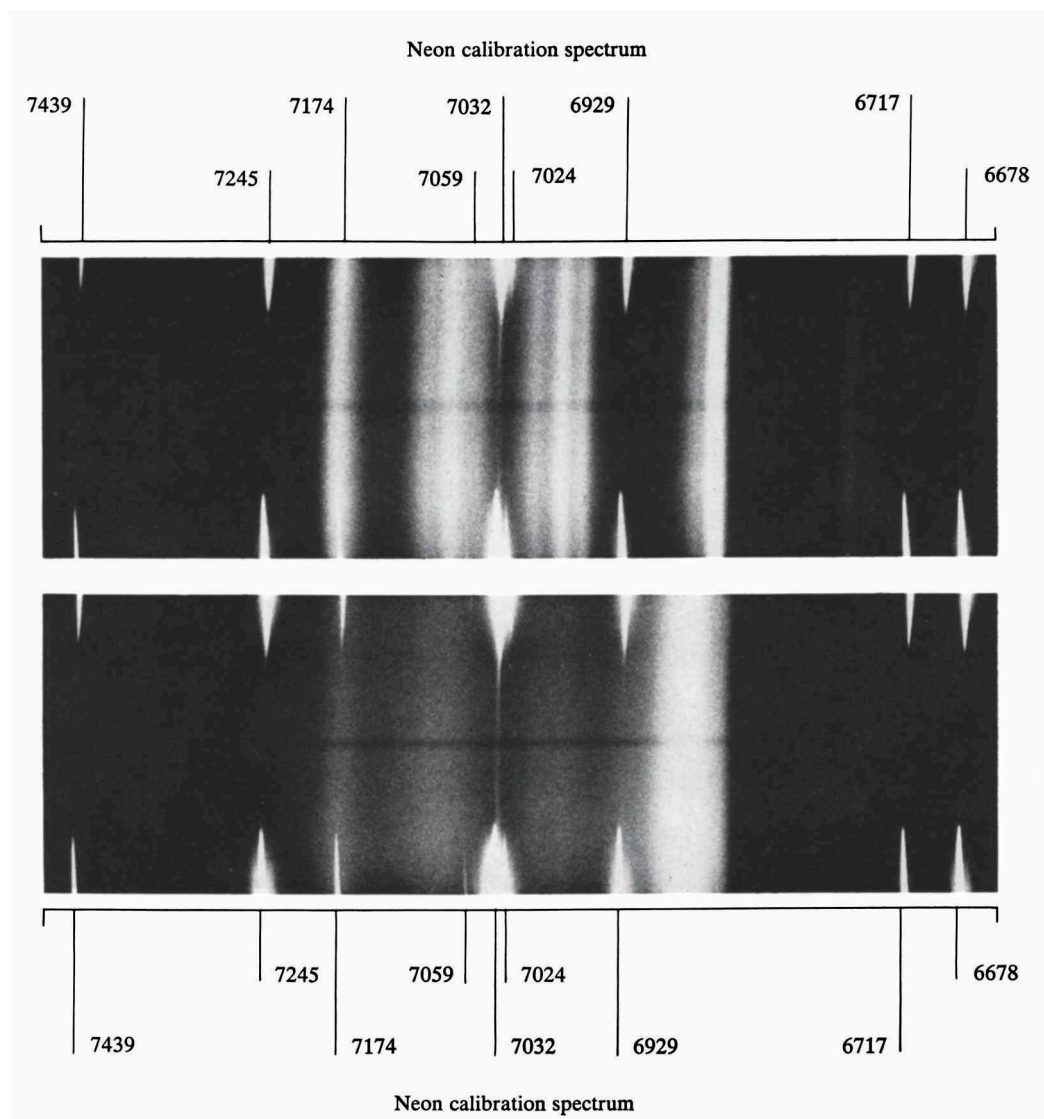


Fig. 7. Comparison of the luminescence spectra of red spinel of the common variety (S 64, upper figure) and of the spineloid pebble from Ratnapura (S 99, lower figure). Excitation by blue radiation. Wavelengths in Ångström Units.

## PRELIMINARY CONCLUSIONS

Having analysed significant spectrographical data, we can summarize our conclusions as follows:

Characteristic wavelengths of luminescence lines of the normal and the anomalous crystals are practically identical in the wavelength-range between 7250 and 6600 Å. As the normal variety of red spinel contains  $\text{Cr}^{3+}$  ions, it follows that:

The anomalous crystal also contains  $\text{Cr}^{3+}$  ions (same distribution of energy-levels characteristic of the ion) and that the crystal field around the chromium ions is closely related:

The crystal lattice is similar to that of the common spinel. On the other hand, differences in intensity of corresponding lines (energy-transitions) are notable (2nd order effect). This shows that ion interactions and the intensities of certain transition processes are significantly different in the normal spinel and in the anomalous crystal.

It is concluded that the structure of the anomalous crystal (S 99), judged on analysis of spectrographical data, is a modification of the normal, chromium containing red spinel: it will therefore henceforward be named, provisionally, 'spineloid'. Its individuality is confirmed by its characteristic spectrum, which differs essentially from the  $\text{Cr}^{3+}$  spectra of known minerals containing this ion.

Finally, concrete spectrographical data, characteristic for this new mineral variety have become available. They make identification of the species possible without any uncertainty. However, it will be necessary to explore other spectral ranges in the same way. The present method allows this to be done in the range between 3800 Å and 12 000 Å.

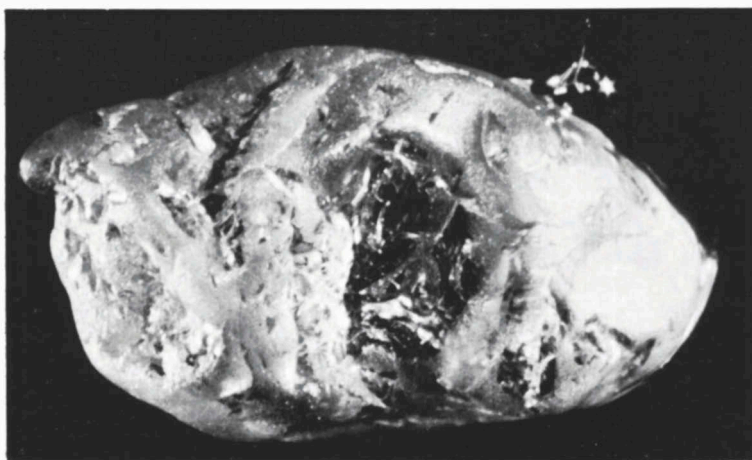


Fig. 8. Grain of the extraordinary variety of red spinel, 'spineloid', from Ratnapura (S 99); reflected light, 20 x.

Table 1. A comparison of the luminescence spectra of red spinel of the normal type, and of a red spineloid crystal, both from the Ratnapura gem gravels of Sri Lanka.

RED GEM SPINEL CRYSTALS (normal type)				RED SPINELOID CRYSTAL (new variety of spinel)			
Line-group	Intensity	Character of spectral lines	Wavelength in Å	Wavelength in Å	Character of spectral lines	Intensity	Line-group
	0.3 0.5 0.8  1.2  0.8	broad, weak broad, weak broad  very broad and diffuse  broad and diffuse	7660 ± 10 7565 ± 10 7472 ± 4  7393 ± 10  7310 ± 6	   7432 ± 5  7375 ± 5 7335 ± 5 7270 ± 5	   broad and diffuse  broad and diffuse broad and diffuse broad and diffuse	   0.2  0.2 0.2 0.3	
B —3 L A B	1.8 5 3	relatively narrow widened widened	7228 ± 2 7178 ± 2 7166 ± 2	7226 ± 2 7179 ± 2 7168 ± 2	broad widened widened	0.7 1.9 2.1	L A B —3 B
B —2 A B C	3.5 6 3.3	widened narrow widened	7098 ± 2 7072 ± 1 7048 ± 2	7096 ± 2 7077 ± 2 7056 ± 3	broad broad broad	2.4 2.3 1.1	A B B —2 C
B —1 A B C	3.5 6.5 4.5 0.6	widened narrow narrow weak, vague	7003 ± 2 6979 ± 2 6961 ± 1 6933 ± 4	7003 ± 2 6981 ± 2 6962 ± 2 6932 ± 2	broad broad broad broad	1.8 2.2 1 1.8	A B B —1 C
B 0 A B C	1.6 2.8  10	widened widened  narrow, sharp band head short wave side. Reversible.	6898 ± 2 6874 ± 3  6857 ± 1	6896 ± 2 6876 ± 2  6856 ± 1	broad, diffuse very intense, broad, diffuse. narrow	6.5 10  3.6	A B B 0 C
B +1 A B C	0.4 0.5 2 1.5 0.8	widened, weak and diffuse. widened narrow, reversible narrow narrow	6787 ± 2 6772 ± 1 6757 ± 1 6742 ± 1 6720 ± 2	6802 ± 3 6776 ± 2 6755 ± 2 6733 ± 3 6721 ± 2	broad, diffuse  broad, diffuse broad, diffuse broad, diffuse broad, diffuse	0.4  0.8 1 0.8 0.4	A B B +1 C
B +2 A B C	0.5 0.8 0.3 0.3	narrow narrow, reversible narrow narrow	6680 ± 3 6656 ± 2 6634 ± 4 6610 ± 2	6682 ± 3 6659 ± 2 6622 ± 4	broad, weak, diffuse. broad broad and diffuse	0.3 0.5 0.4	A B B +2 C
B +3	0.4 0.2	broad broad	6571 ± 2 6524 ± 2				



## Explanation of Table 1

*Wavelength* — Wavelengths are expressed in Ångström units, because this unit is widely used in the mineralogical sphere. The standard unit is the nanometer ( $10^{-9}$  m): it is equal to 10 Ångströms. Wavelengths, indicated in the table, are the wavelengths of the maximum intensity in each (broadened) line.

*Character of spectral lines* — As we are dealing with ion spectra in a solid substance, most luminescence lines are spread out in width and sometimes show a hyperfine structure. This is a consequence of vibrational effects, and splitting of energy levels in a number of sublevels. The broadening of lines diminishes the accuracy of wavelength determination.

It would be interesting to study luminescence at low temperatures (of the order of 80°K or lower); it is probable that the luminescence lines would be very much narrower in that case.

*Intensities* — The intensities given in the table are determined from the density of photographic line impressions on Kodak high speed infrared film (Type 2481, see Kodak Publication P-9, p. 24 d). If the sensitivity is taken as 10 at 700 nm, it will be only about 6 at 650 nm, and 4.7 at 600 nm. For this reason the intensities of lines under 700 nm wavelength are tending to be too low.

*Line group* — If the luminescence lines of common red spinel are viewed through a small-dispersion spectroscope, they appear as a rather spectacular *grouping of wide and diffuse bands* centered around a narrow and very intense line. These bands have been named 'organ pipes' by B. W. Anderson (see Webster, fig. 482, p. 668). When a spectrogram is taken with a spectrograph of a sufficiently large dispersive power and resolution, these bands are seen to consist of a number of narrower lines: they are *multiplets*.

In order to be able to compare the particularities of the spectra of the common variety of spinel and the new variety, which the author has named provisionally 'spineloid', the structured bands are indicated by letters and numbers as follows: As there seems to be a central symmetry around the band, which contains the (resonance) line of the highest intensity, this band was designated as B O. Going from this group to the higher wavelengths (lower quantum energies), the bands (line groups) are indicated by B —1, B —2, etc. Similarly, the bands (line groups) of lower wavelengths and higher quantum energies are indicated by B +1, B +2, etc.

The multiplets in each line group are also of a distinctive character: the most intense lines *seem* to appear most frequently in groups of three (triplets), or in some cases as doublets. The components of these apparent multiplets are designed by the letters, A, B and C in order of diminishing wavelength. Some prominent lines, which for the present appear to be single, are marked with an L.

*Arrangement of data* — In order to enhance the importance of high resolution spectrography and to demonstrate the real significance of the analysis of multiplet structures, which may lead to the discovery of otherwise hidden similarities in crystal structures, the data obtained from the spinel and spineloid crystals were grouped as explained above and were then placed side by side in the table. This arrangement reveals very clearly the similarity (near identity) of the energy-levels of the  $\text{Cr}^{3+}$  ion in both lattices: the differences in *wavelengths* of corresponding lines are small in the main groups. It becomes thus clear, that the spineloid is indeed to be considered as a *variety of spinel*.

On the other hand, the arranged data expose the considerable differences in line-intensity distributions in corresponding multiplets of the spinel and the spineloid. It is the nature of these differences — which are a consequence of alterations in ion interactions and probability patterns of transitions — that is significant for the definition of the spineloid.

## Evaluation of results, discussion and conclusion

In the preceding section, dealing with the results of the main analysis work on which this article is based, i.e. the application of high-resolution spectrography to analysis of energy levels of active ions in crystals, we have demonstrated the possibility to determine a new crystallographic variety of an important mineral like spinel. After this discovery, we will first see whether differences can be found between the more obvious physical properties of the common red spinel and those of the spineloid.

### COMPARISON OF COMMON PHYSICAL PROPERTIES OF THE NORMAL RED SPINEL AND THE SPINELOID

The author disposes of only one fragment of a spineloid crystal in the shape of a pebble, weighing but 0.45 carats, which was separated from roughly a thousand similar grains of common spinel. This is significant for the relative rarity of the new spinel variety. A photomicrograph of the spineloid grain is shown in fig. 8. Because of the uniqueness of the sample S 99, it was not possible to carry out tests of a more or less destructive nature. Thus, for the present, we will have to content ourselves with the following comparative data:

*Density* — The density of the spineloid, as determined by the author with the aid of a heavy liquid — in this case a hydrated mixture of thalliumformiate and thalliummalonate (Clerici's solution) — was 3.61. If we compare this to the densities, measured by Dr Zwaan for the spinels Bode A-C (see p. 9) which are, respectively 3.579, 3.592, and 3.587 and to the density of RGM 150 888 — 3.603 —, we see that the spineloid has a slightly higher density.

*Colour* — The colour of the spineloid pebble is best described as 'mallow purple': for comparison of colours, use was made of the Colour Chart of the Royal Horticultural Society; its list of cross-references gives many colour indications derived from mineral names (R.H.S. Chart). In artificial — incandescent — light, the colour of the spineloid appears distinctly more reddish (72D of the R.H.S. Colour Chart) than by daylight (73C of the same chart). By comparison, the colour of the cut spinel RGM 150 888 was classified as 'spinel red' (54B of the R.H.S. Colour Chart).

*Optical properties* — The normal spinel is invariably isotropic. When examined between crossed polarizers (Zeiss polarization microscope) our spineloid appeared to be practically isotropic. There may be a very slight degree of double refraction *locally* in the clear interior, but the magnitude of the effect is very small. Crystals of corundum, painite or taaffeite (see Webster, 1962, pp. 274, 290) are anisotropic.

*Cleavage* — Microscopical faults, observable in the interior, seem to lie in the direction of octahedral planes. They are cracks, rather than perfect cleavages. Normal spinels show only imperfect octahedral cleavages.

*Lattice constants* — X-ray diffraction measurements were carried out under the auspices of Professor Hartman of the Institute of Geology and Mineralogy of the University of Leiden. A crystal diffraction pattern (Weissenberg method) shows, that the spineloid has a normal spinel structure; the unit cell dimension  $a_0 = 8.082 \text{ \AA}$ . This compares well with the value of  $8.09 \text{ \AA}$ , characteristic for the normal stoichiometric  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel. It is in accordance with the preliminary conclusions on p. 15. Apparently, the subtle differences in crystal lattice structure, such as would be caused by the substitution of small amounts of  $\text{Cr}^{3+}$  ions (even in different locations), does not show up in a prominent way with this analysis method, as it does with the spectrographical method.

#### SYNTHESIS OF THE CHARACTERISTICS OF THE SPINELOID

From the assembled data, given in the preceding part of the paper, we will synthesize a picture of the distinctive properties of the spineloid. This sort of evaluation involves much theory of solid state physics. Of necessity, it must be kept short to fit the general trend of the article. For the purpose of a systematic comparison of properties, we will follow a definite sequence:

*Structural details* — The spineloid is optically isotropic; the lattice is of the spinel type, and the unit cell dimension  $a_0$  does not deviate significantly from the normal value for  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel.

*Luminescence spectrum in the red region* — From the pattern of wavelengths, corresponding to a system of energy levels, it is clear, that the main component lines originate in  $\text{Cr}^{3+}$  ions, which are surrounded by six oxygen ions (octahedral field). The energy levels are characteristic for a magnesium-aluminium spinel (p. 15). Energy transitions, taking place between the  $^4\text{A}_2$  ground state of the ions and the excited  $^2\text{E}$  states, give rise to typical sequences of lines and composite sidebands. Some lines are caused by interactions of paired ions (Landé sequence). Typical predominant R doublets — observable in corundum (ruby), emerald and alexandrite (pseudo-hexagonal properties) — are absent. However, the intensity distribution of the luminescence lines of the spineloid deviates considerably from the normal spinel line intensity distribution; also, the lines are generally wider and more diffuse. This is indicative of the presence of  $\text{Cr}^{3+}$  ions in different sites, with modified interactions. Vibronic sidebands are more prominent.

*Luminescence in the green region* — In earlier stages of the research of the cathodo-luminescence of the spineloid, the presence of a rather intense, partly structured band in the range between  $5000 \text{ \AA}$  and  $5470 \text{ \AA}$ , was noted. This band is most probably caused by  $\text{Mn}^{2+}$  ions in  $\text{Mg}^{2+}$  sites.

*Significance of spectrum* — The spectral type of the spineloid must be characteristic for the variety: the spectrum of this one grain in a thousand is significantly different from the uniform spectrum, characteristic of the rest. No intermediate spectral types were found.

*Colour* — The colour of the spineloid is more violet than the normal  $\text{Cr}^{3+}$  spinel's

colour. This may be due to the presence of ions of transition metals, such as Fe or Mn ions of different valencies. The colour of the  $\text{Cr}^{3+}$  containing spinels is also dependent on the molar ratio between MgO and  $\text{Al}_2\text{O}_3$ : synthetic spinels with a molar ratio between 1 : 1 and 1 : 1.2 are pink: with a ratio of 1 : 1.5 they become greyish-green. If the ratio exceeds 1 : 2, the spinels are dark green in colour (see Groem-Gržimailo, 1970, p. 302).

*Broad absorption band* — Chromium containing crystals show a characteristic, broad absorption ( $^4\text{A}_2 \rightarrow ^4\text{T}_2$  (F) band among others) in the green region. The spineloid also shows a broad absorption between 5940 and 5320 Å with its maximum at 5520 Å (18 116 lines per cm). It is wider than the corresponding band of the common red spinel, which is situated between 5780 and 5200 Å; with its maximum at 5500 Å (18 180 lines per cm). In the spineloid, the maximum is displaced towards the red.

*Unit cell dimension* — The value for  $a_0 = 8.082$ , as determined by Professor Hartman, does not deviate significantly from the value of 8.09, characteristic for the MgO.  $\text{Al}_2\text{O}_3$  spinel.

*Impurities of a non-essential nature* — The iron content of the spineloid must be very small, as the intensity of its luminescence is very high, and comparable to that of a pure ruby.

#### COMPARISON OF PROPERTIES

We will first systematically enumerate the properties of a number of possible varieties of spinels and crystals with spinel-like lattices, containing  $\text{Cr}^{3+}$  ions (and other ions). They will then be compared to the properties of the spineloid as evaluated in the preceding section.

##### *Model A*

*Structural details* — A normal, stoichiometric  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  (1 : 1) spinel (class of symmetry  $\text{O}_h^7$ ) containing  $\text{Cr}^{3+}$  ions in non-deformed octahedra of  $\text{O}^{2-}$  ions (co-ordination number 6). The  $\text{Cr}^{3+}$  ions replace  $\text{Al}^{3+}$  ions of a slightly smaller (by 0.08 Å) radius.

*Red luminescence spectrum* — The spectrum of this variety is described on p. 13. It is due to transitions between the ground state  $^4\text{A}_2$  and the excited  $^2\text{E}$  states: doublets and quadruplets appear in symmetrically arranged groups with a definite intensity-distribution.

*Luminescence in the green region* — The normal red spinel does not show significant luminescence in the green region, not even with intense cathode-ray excitation.

*Significance of spectrum* — This is proved by the enregistration of a great number of spectra of normal spinel crystals. They are practically identical in the range

studied. In some, having a higher chromium content, interactions can take place between pairs of Cr ions; this gives rise to emissions in the farther infrared range.

*Colour* — The colours are spinel red of varying intensity.

*Broad absorption band* — There are two characteristic bands:

1) the  ${}^4A_2 \rightarrow {}^4T_2$  (F) band centered around 5500 Å (18 180 lines per cm), with a separation of 1800 lines per cm; 2) the  ${}^4A_2 \rightarrow {}^4T_1$  (F) band, centered around 3950 Å (25 310 lines per cm).

*Unit-cell dimension* — This value is 8.09 Å

*Impurities of a non-essential nature* — The iron content of the red gem spinel is very small, but variable. The spinels of light colour show the most intense luminescence, they have the lowest iron content.

### *Model B*

*Structural details* — A stoichiometric or near stoichiometric  $MgO \cdot Al_2O_3$  spinel (molar ratio between 1 : 1 and 1 : 1.2). The spinel lattice allows important defects. It has been proved, by EPR-analysis (Electron Paramagnetic Resonance), that the  $Cr^{3+}$  ion can occupy two locations in the lattice of natural spinel: one is the normal  $Al^{3+}$  position (undistorted octahedral field), the other in a distorted octahedral field (positions normally empty). The co-ordination number is 6 in both cases. The ions in the distorted field ( $Cr^{3+}(6)d$ ) seem to be located in polyhedral space-groups; interactions with the ions in the normal field ( $Cr^{3+}(6)n$ ) are notable.

*Red luminescence spectrum* — This spinel variety possesses a more complex luminescence spectrum, showing the basic energy levels of  $Cr^{3+}(6)$ , but with a different intensity distribution. Spectral lines might be significantly broadened by the effect of the distorted field around the  $Cr^{3+}(6)d$  ions, and by interactions.

*Luminescence in the green region* — This spinel variety does not show any significant luminescence, if no strange ions are present.

*Significance of spectrum* — Due to the appearance of the  $Cr^{3+}(6)d$  ions in definite polyhedral groups, the spectrum is specific for this spinel type.

*Colour* — As usual, the colour is pink.

*Broad absorption bands* — There is no important change in width or position of the  ${}^4A_2 \rightarrow {}^4T_2$  (F) band and the  ${}^4A_2 \rightarrow {}^4T_1$  (F) bands.

*Unit cell dimension* — This value does not deviate significantly from the value of 8.1 Å.

*Impurities of a non-essential nature* — The iron content should be small to produce a high-intensity spectrum, especially as the chromium content might be higher than in the spinel A.

### Model C

*Structural details* — A stoichiometric  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel as A, with  $\text{Mn}^{2+}$  ions in  $\text{Mg}^{2+}(4)$  positions, and also  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions in the  $\text{Al}^{3+}(6)$  positions. The ion-radius of  $\text{Mn}^{3+}(6)$  is 0.66 Å, and the radius of the  $\text{Mn}^{4+}(6)$  ion is 0.60 Å. The ion radius of the  $\text{Cr}^{3+}(6)$  ion is 0.63 Å. Spinel of this type have been produced by the Verneuil method (see Groem-Gržimailo, 1970, p. 306).

*Red luminescence spectrum* — The spectrum of this spinel is caused by the  $\text{Mn}^{3+}$  ion ( $3d^4$  electron configuration) and the  $\text{Mn}^{4+}$  ion ( $3d^3$  configuration, like  $\text{Cr}^{3+}$ ). The  $\text{Mn}^{4+}$  ion causes a luminescence, very similar to that of the  $\text{Cr}^{3+}$  ion: there are two groups of narrow emission lines centered around 6870 Å; the  $\text{Mn}^{3+}$  ion causes wide bands. These two spectra would appear superposed.

*Luminescence in the green region* — The  $\text{Mn}^{2+}(4)$  ion causes a broad band in the yellow-green region. Such a band is observed in the spinels from Kangaiyam (India), when excited with cathode-rays.

*Significance of spectrum* — Important variations in composition are possible and the spectrum would not be essentially characteristic.

*Colour* — In larger concentrations, the colour of these spinels, caused by Mn, is a brownish pink with a violet tinge. With low concentrations of Mn, the colour may be yellowish.

*Broad absorption bands* — Mn spinels show a broad absorption in the green region; it is composite, and shows broad maxima: 5600 Å and 4900 Å of the  $\text{Mn}^{2+}$  ion, and 4800 Å for the  $\text{Mn}^{3+}$  ion.

*Unit cell dimension* — This value does not deviate significantly from the value of 8.1 Å.

*Impurities of a non-essential nature* — The iron content should be small to produce a high intensity luminescence spectrum.

### Model D

*Structural details* — A substantially non-stoichiometric spinel  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  with a molar ratio between 1 : 1.2 and 1 : 1.4, containing  $\text{Cr}^{3+}(6)n$  ions, replacing the  $\text{Al}^{3+}$  ions in normal positions.

*Red luminescence spectrum* — It should not deviate significantly from the spectrum of spinel A, as the field around the  $\text{Cr}^{3+}(6)$  ions is not very much influenced.

*Luminescence in the green region* — This spinel variety, if no active ions of other elements are present, should not show any luminescence in this spectral region.

*Significance of spectrum* — The spectrum would be characteristic for  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel with  $\text{Cr}^{3+}(6)$  ions; the deviations from the stoichiometric molar ratio should

only show as third order effects in the red luminescence spectrum.

*Colour* — In the molar range defined, the colour would still be pink; near a molar ratio of 1 : 1.5 it would change to a greyish green. The colour is influenced by the valency of chromium-ions in other positions.

*Broad absorption bands* — With varying molar ratio, the absorption maximum in the  ${}^4A_2 \rightarrow {}^4T_2$  (F) band does not shift from its original position at 5500 Å. The maximum of the  ${}^4A_2 \rightarrow {}^4T_1$  (F) band shifts from 3950 Å to approximately 4050 Å. In addition, with increasing  $Al_2O_3$  content, a third band appears on the red side at 6600 Å; it shifts significantly to the violet with increasing  $Al_2O_3$  content. It merges with the  ${}^4A_2 \rightarrow {}^4T_2$  (F) band. The origin of this band has not been satisfactorily explained, up till now. The total effect, however, is a general widening of the absorption band in the green, accompanied by a slight shift of the red limit towards longer wavelengths.

*Unit cell dimension* — It might deviate from the value of 8.1 Å for spinel. There is a lack of data in this respect on synthetic spinels.

*Impurities of a non-essential nature* — The iron content must be low to produce a luminescence spectrum with a high intensity. Natural spinels with an increased content of  $Al_2O_3$  have been observed. In spite of many attempts, the author did not succeed in obtaining samples of red synthetic spinels for comparative analyses.

### Model E

*Structural details* — The  $\gamma$ -modification of corundum, which is stable up to a temperature of 900°C, has a lattice of the spinel type. It appears possible that such a modification could exist, in which  $Cr^{3+}$  ions replace part of the  $Al^{3+}$  ions.

Very little can be said about the spectral properties of this  $Cr^{3+}$  containing corundum modification in the absence of experimental data. As the structure is of the spinel type and the  $Cr^{3+}$  ions would occupy  $Al^{3+}$  sites, its luminescence spectrum should resemble the spectrum of the normal  $MgO \cdot Al_2O_3$  spinel and show the Landé sequence of lines, due to interaction of paired ions.

*Unit cell dimension* — Precise determinations have been made by Beljankin and Dilaktorski (1932, p. 242); the  $a_0$  value is 7.91 Å. This differs significantly from the value for  $MgO \cdot Al_2O_3$  spinel (8.09 Å).

Other properties, determined by the same authors (op cit.) are: 1) the density of  $\gamma$ -corundum — 3.647 — is higher than the normal density of Mg-spinel (see p. 9); 2) the index of refraction is 1.696 in sodium D light, this is lower than the corresponding index for Mg-spinel (see p. 9). The  $\gamma$ -corundum studied was not of natural origin. The modification is stable up to 950°C, however, and perhaps to 1200°C.

A further cubic modification, the  $\zeta$ -modification, having a unit cell dimension of 7.90 Å, is stable up to 1600°C. The possibility of natural occurrence in mixed lattices may not be entirely neglected.

## DISCUSSION AND CONCLUSION

After having summed up the characteristics of the possible 'model' structures A to E, we will compare their data patterns with the pattern of spineloid (see p. 19), based on experimental data.

Variety A is the normal spinel, which possesses a characteristic spectrum, essentially different in its intensity distribution from the spectrum of the spineloid.

Variety D, a spinel with a non-stoichiometric composition (excess of  $\text{Al}_2\text{O}_3$ ), would show variable properties of colour, density, refractive index and unit cell dimension  $a_0$ , but the luminescence in the red wavelength range would not differ much from that of  $\text{Cr}^{3+}$  in common spinel. By itself, it does not make a very suitable model.

Variety E is rather improbable as a model: the unit cell dimension of  $\gamma$ -corundum is different from the one of spineloid; spectral properties are unknown at present and the occurrence in nature is problematical.

Variety C shows some interesting characteristics, which certainly have a relation with measured properties of the spineloid. However, as pure model it would not fit, because the wavelengths in the red luminescence spectrum would be different from the spinel/spineloid pattern and the spectrum would probably be variable because of valency changes of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions (possible photochemical effects).

Variety B seems to be the best fitting model. It provides an explanation for nearly all particularities of the spineloid, in particular the composition of its characteristic spectrum in the near infrared range. If we assume the presence of Mn as  $\text{Mn}^{2+}(4)$ , probably accompanied by  $\text{Mn}^{3+}(6)$  and  $\text{Mn}^{4+}(6)$ , as explained in model C, then the luminescence observed in the green spectral region, the deviation in colour, the extended width of the  ${}^4\text{T}_2(\text{F})$  chromium band, and a shift of the absorption-maximum to the red would all be accounted for.

On the basis of the assembled evidence — though not complete — we reach the following conclusion about the probable structure of the spineloid:

The spineloid is a stoichiometric or nearly stoichiometric  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel with a relatively high  $\text{Cr}^{3+}$  content, causing the characteristic spectrum, and with admixed  $\text{Mn}^{2+}$  ions in  $\text{Mg}^{2+}$  sites; also  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions in  $\text{Al}^{3+}$  sites.

Characteristic is the *ordered* (non-statistical) distribution of the trivalent chromium ions over two types of site, having different separations of the  ${}^2\text{E} - {}^4\text{A}_2$  levels and different split  ${}^2\text{E}$  levels; giving rise to definite interaction patterns. The normal site is that of the  $\text{Al}^{3+}$  ion in its normal position in the center of six  $\text{O}^{2-}$  ions in a non-deformed octahedral position. In the other type of site, the  $\text{Cr}^{3+}$  ion is also surrounded by six  $\text{O}^{2-}$  ions but apparently in a deformed octahedral position. These ions seem to appear in pairs, which form ordered polyhedral space patterns in the spinel lattice. Because of this, there is a definite pattern of interaction between the ions, which leads to a typical luminescence spectrum (a wavelength-intensity relation characteristic for a variety) especially as regards the appearance of pair lines in the near infrared region. This systematical pairing of ions in the spineloid is different from the random pairing effects in the common spinel.

The  $\text{Mn}^{2+}(4)$  ions cause the green luminescence (cathodoluminescence observed in the spineloid; also in the Kangaiyam spinels).  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions in



$\text{Al}^{3+}(6)$  sites could modify the red luminescence spectrum, but their influence would be variable.

As a third factor, the molar ratio between  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ , even in the restricted range between 1 : 1 and 1 : 1.2, may not be neglected in view of its possible effects on the order of  $\text{Cr}^{3+}$  ions. It would also be a variable factor.

All in all, the method of optical high-resolution spectrography proves to be a very sensitive one. It is especially suited to the detection of varieties of crystals, characterized by ordered patterns of substituting ions and definite interaction processes. The method should preferably be used in combination with EPR-analysis. It will certainly, with extended application, give rise to many more discoveries.

The exact nature of the ordered distribution of the different types of  $\text{Cr}^{3+}$  ions has still to be revealed. For this, it would be necessary to develop mathematical models, and carry out a program of calculation for comparison with the actual data.

## Summary

Advanced spectrographical methods of analysis used in solid state physics, and also in astrophysics, can be adapted and developed into a practical research method in mineralogy. Its application promotes discovery and determination of new varieties of minerals.

In this study, the new method — developed by the author — was applied to red magnesium spinels from the gem gravels of Ratnapura in Sri Lanka (formerly Ceylon). In order to provide a sound statistical basis, spinels from other sources were also analysed. In the course of investigations, a new variety of red spinel was discovered.

As an introduction, physical principles of absorption and luminescence of optically active ions in crystal lattices are briefly reviewed. The rôle of the trivalent chromium ion as a sensitive indicator of energy states in specific crystal fields is brought forward. Its luminescence spectrum is a conform representation of these energy states. Essential for the new method is the excitation of luminescence by means of a high energy-density flux of blue radiation (continuous between 4000 and 5800 Å), and the use of a spectrograph with an effective range between 3800 and 12 000 Å, of adequate power of resolution (more than 30 000) and dispersion (better than 30 Å per mm at 7000 Å in the focal plane of the camera). Spectrograms, enregistered on suitable photographic material under these conditions, reveal multiplet structures in the striking luminescence spectrum of spinel in the near infrared range studied (6500 to 7600 Å).

Numerical evaluation of these spectrograms leads to conclusions about characteristic energy levels of the chromium ion in the spinel lattice (wavelengths), and about characteristic probabilities of energy transitions (intensities of spectral lines). In an earlier stage of development, the new method made the discovery of a variety of fluorapatite (europiumapatite) and of scheelite (erbioscheelite) possible (Lagerwey, 1973). The main subject of this article is the investigation of red spinels from the Ratnapura gravel pits. Examination of a considerable number

of spinel grains revealed the presence (less than one per thousand) of a spinel like mineral, which possesses a luminescence spectrum of trivalent chromium significantly different from the spectra of all known chromium-containing minerals. Highly resolved luminescence spectrograms were made of a number of common red spinels from Ratnapura and — for the purpose of comparison — of similar spinel crystals from Kangaiyam (Madras province, India), as well as of some magnificent cut spinels of the collection of Mr Bode of The Hague (Bode A-C), which is displayed in the Rijksmuseum van Geologie en Mineralogie.

In this manner, data of statistical significance were gathered, which are proof of the uniformity of the luminescence spectra of the normal variety of red spinel in the range between 6500 Å and 7600 Å. The resolved spectrum of the extraordinary stone, on the contrary, while showing the same wavelength pattern to all practical purposes, possesses a completely different intensity distribution of the spectral lines. This means that, while the pattern of energy levels of the  $\text{Cr}^{3+}$  ions is similar for both varieties of spinel, the intensities of the various transitional processes in single and paired ions are different in the spineloid. Therefore, the new mineral must be a spinel of a characteristically modified structure. Fig. 7 of the paper shows the spectra of the normal and of the extraordinary variety of spinel superposed, to demonstrate resemblances and differences. In table 1, detailed numerical data about wavelengths, character and intensities of spectral lines are given for both varieties; these data are suitable for identification of the variety.

Results of the spectrographic measurements, combined with those of other physical measurements, as available and realizable in the present stage, are evaluated and a picture of the distinctive properties of the spineloid variety is synthesized. Its characteristic pattern of properties is then compared to patterns, which can be assigned, on the basis of our present knowledge of spinel type lattices, to six different models of spinel varieties containing chromium or manganese ions. By a process of elimination it was then possible to reach a tentative conclusion about the nature of the spineloid.

The spineloid is a stoichiometric or near stoichiometric  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel with a relatively high  $\text{Cr}^{3+}$  content, causing the characteristic spectrum, and with admixed  $\text{Mn}^{2+}$  ions in  $\text{Mg}^{2+}$  sites; also  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions in  $\text{Al}^{3+}$  sites. In the spineloid, the trivalent chromium ions occupy two types of site in the lattice; they also appear in pairs, which are arranged in regular polyhedral space patterns in the spinel lattice. This explains the appearance of characteristic pair lines in the spineloid spectrum in the near infrared range. The presence of ions of bivalent, trivalent, and quadrivalent manganese manifests itself by luminescence bands in the green and red spectral regions. A limited deviation from the stoichiometric molar ratio could have an influence on the appearance of regular configurations of trivalent chromium ions.

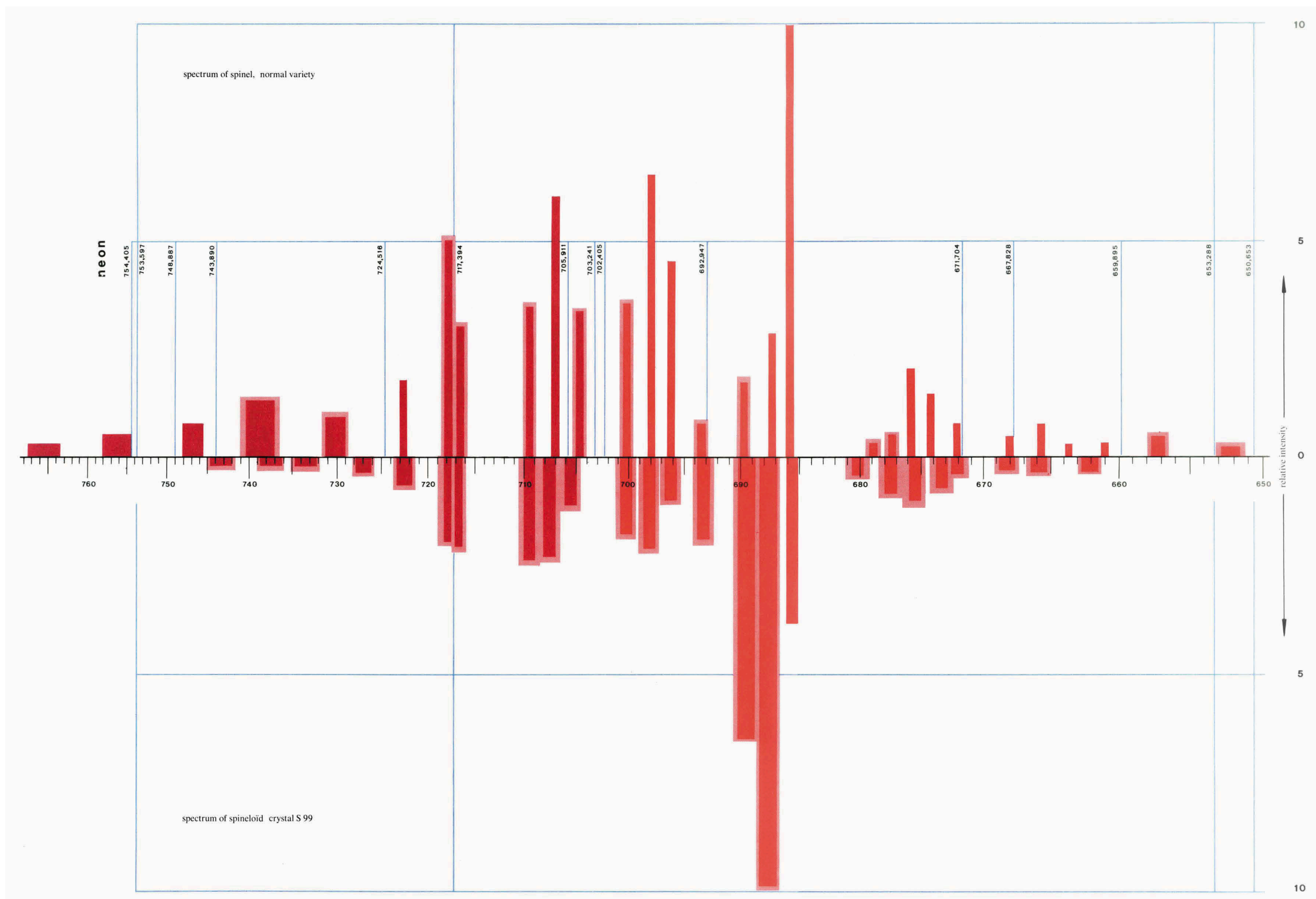
The availability of only one grain of spineloid of 0.45 carats seriously restricted the range of analyses and in consequence many complementary data are lacking. It is hoped, however, that with the aid of the data provided other specimens of the spineloid will eventually become available for research.

The results of the present investigations demonstrate the possibilities of the new method of spectrographical analysis: continued application on a wider scale will almost certainly lead to the discovery of a whole series of varieties of minerals.

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Diagram, representing multiplet structures of spectral lines in the range between 6500 and 7600 Å, characteristic of red spinel of the normal variety and those of the spineloid crystal S 99, calibrated with the spectrum of neon. Wavelengths expressed in nm.