

A Russian Maxixe beryl?

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Abstract: Maxixe beryl has a deep blue colour, which fades upon extended exposure of the crystal to daylight. In a 1976 publication a colourless Russian beryl was reported to contain a considerable amount of NO₂. The published EPR spectrum of this beryl is similar to that of a bleached Maxixe beryl. Analysis of the colour centres of Maxixe beryl and the artificially created Maxixe-type beryl indicate that samples of this Russian beryl could display the blue colour of Maxixe beryl after irradiation.

Keywords: EPR, Maxixe beryl, NO₂ in beryl

Introduction

The observation of NO₂ impurities in a colourless Russian beryl by Electron Paramagnetic Resonance (EPR) spectroscopy (Sukharzhevskii, 1976) suggests that this Russian beryl may have had (and can again obtain) the features of the rare Maxixe beryl found around 1917 in Brazil. This possibility is based on a study of the creation and decay of the colour centre in the Maxixe beryl. Comparison of these processes is also made with the behaviour of the colour centre in the Maxixe-type beryl which appeared on the gemstone market around 1973.

A crystal of beryl (Be₃Al₂Si₆O₁₈) consists of silicate rings stacked upon each other, like stacks of doughnuts. The holes in the middle form channels stretching throughout the crystal structure. These channels are parallel to the *c*-axis of the beryl crystal and have a diameter which varies between 2.8 Å in the rings and 5.1 Å between the rings. Neighbouring stacks are held together by Be and Al ions. Impurity ions like Fe, Mn and Cr can replace Al or Be ions in natural beryl crystals. Relatively large

amounts (often more than one weight %) of other impurities, mainly alkali ions and water, but also CO₂ and CH₄ molecules, can be located in the channels.

Chemical bonds in molecules (such as CO₂), ions (such as CO₃²⁻), and crystals usually contain paired electrons. NO₂ and NO₃ molecules are exceptions with unpaired electrons. Unpaired electrons are also a result from irradiation which can remove one electron (as in CO₃⁻) or add one electron (as in CO₂⁻). EPR spectrometers are used to detect such unpaired electrons and study their behaviour. They can also be used to study the unpaired electrons in paramagnetic ions (such as Fe³⁺ and Cr³⁺). When a strong magnetic field is applied, the spin of the electrons will be oriented parallel or antiparallel to the magnetic field. These orientations have different energy levels and transitions between them occur in the microwave region. The EPR spectrometer registers the microwave absorption of the unpaired electrons. The spectrum is obtained by keeping the microwave frequency constant and changing the magnetic field.

Maxixe beryl and Maxixe-type beryl

Maxixe beryl was first described in the scientific literature by Wild (1933), who stated that the crystal had been found 15 years earlier in the Maxixe mine. This beryl had a deep blue colour, which faded when the crystal was kept for many days in daylight. It is strange that there are no earlier reports about this unusual beryl, after it had caused the gemstone dealers such disappointment. The samples investigated by Wild had been kept in the dark since about 1917 and had not lost their blue colour. More detailed investigations of this material were made by Schlossmacher and Klang (1935) and by Roebbling and Tromnau (1935). Schlossmacher and Klang (1935) describe the location of the Maxixe mine in Minas Gerais, Brazil, and state that the mine was closed when the loss of colour caused a lot of trouble. One other of Wild's samples has been described in detail by Schiffman (1977). No other beryl with the same properties as Maxixe beryl has since been reported.

In 1972–1973 more beryl crystals of an intense blue colour appeared on

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the gemstone markets, but the initial enthusiasm for these beautiful stones changed to disappointment when it was found that their colour also faded upon extended exposure to daylight in shop window displays. Nassau *et al.* (1976) investigated these crystals and established that they have the opposite dichroism to that of aquamarine. The blue colour of the new beryl is carried by the ordinary ray, while that of aquamarine is carried by the extraordinary ray. Nassau *et al.* (1976) called these new beryls Maxixe-type beryls because their optical absorption spectra contained similar, but slightly different, absorption bands to those from the rare Maxixe beryl. They were also able to create similar blue crystals by irradiation of some other beryls. As will be seen below, this should be possible when the beryls contain enough carbonate ions.

Origin of the blue colour

The different colours of beryl are usually related to paramagnetic ions (iron, manganese, chromium, vanadium) substituting for aluminium in the octahedral sites between the stacks of silicate rings in the beryl crystal structure. However, Maxixe beryl has a very low content of such ions (Roebing and Tromnau, 1935) and the unusual blue colour centres of Maxixe and Maxixe-type beryl are instead located in the beryl channels.

Using EPR spectroscopy, Andersson (1979) determined that the colour centre in Maxixe beryl is the NO_3 molecule, while the colour centre in Maxixe-type beryl is CO_3^- . Since these centres have the same number of electrons in the same molecular orbitals (that is they are isoelectronic), their optical absorption spectra are very similar. However, their EPR spectra are different because the nuclei of the colour centres interact differently with the unpaired electron. The oxygen and carbon nuclei of CO_3^- have no influence on the EPR spectrum, but the nitrogen nucleus of NO_3 splits the EPR signal into three lines. It is therefore easy to separate Maxixe and Maxixe-type beryl by EPR spectroscopy.

Both the NO_3 and CO_3^- groups (radicals) are planar and fit in the widest part of the beryl channel where they are oriented with their trigonal symmetry axis parallel to the crystal *c*-axis. This well-defined orientation gives rise to the strong pleochroism of the blue colour.

Creation of NO_3 and CO_3^- colour centres in beryl

Nassau *et al.* (1976) concluded that the blue colour centre in Maxixe-type beryl is created by irradiation while the Maxixe colour centre is of natural origin. Different possibilities of how CO_3^- and NO_3 radicals could be created in beryl will now be considered.

One possibility is that CO_3^{2-} and NO_3^- ions existed in the original melt and were trapped in the channels of the beryl crystal during its formation. An electron can be removed from each of these ions by irradiation to create CO_3^- and NO_3 . The released electron can be caught by an impurity proton to form a hydrogen atom. Such atoms have been detected in both Maxixe and Maxixe-type beryl by EPR. If this scheme is correct, it can be concluded that both colour centres have been created by irradiation.

A second possibility is that CO_2 and NO_2 molecules were trapped from the original melt during the beryl crystal formation. Wood and Nassau (1967) observed the optical absorption of CO_2 in many beryl crystals and Andersson (1979 and 2010) observed the EPR signal of NO_2 in Maxixe beryl. It has been shown that H_2O molecules can diffuse in the beryl channel (Fukuda, 2009). If a water molecule enters a wide portion of the channel containing a NO_2 molecule, it can combine with this molecule to form NO_3 . The hydrogens are split off as single atoms, which have been detected in the EPR spectrum of Maxixe beryl. The probability that this combination of molecules will happen may be very small, so that it could have taken many thousands of years until a sufficient number of stable NO_3 molecules were created to give the Maxixe beryl its intense blue colour. This process was

proposed by Andersson (2008) to explain the existence of NO_3 in natural beryl crystals. The corresponding process forms CO_3^{2-} in beryl containing CO_2 and in this case the hydrogen is split off as protons. Irradiation creates the Maxixe-type colour centre CO_3^- and the released electron is captured by a proton to form a hydrogen atom.

A third possibility is that OH^- ions diffuse in the structural channel and combine with CO_2 or NO_2 to form CO_3^{2-} or NO_3^- . This possibility has been discussed in detail by Andersson (2006). As in the first possibility, irradiation is needed to create the Maxixe beryl.

Decay of the NO_3 and CO_3^- colour centres

Nassau *et al.* (1976) found that the colour of both Maxixe beryl and Maxixe-type beryl disappeared when the crystals were exposed to daylight for one week or were heated to 200°C for one hour. They observed that while the colour of Maxixe-type beryl was created in one single process, its decay exhibited one fast and one slow component. Edgar and Vance (1977) found that the decay of the CO_3^- EPR signal upon heating of Maxixe-type beryl at 175°C correlated very well with the decay of the optical absorption, while the decay of the hydrogen atom signal was less pronounced in the initial stage.

Both Maxixe and Maxixe-type beryl contain hydrogen atoms which are stable at room temperature, which is rather unusual. The hydrogen atom easily dissociates into a proton and an electron. The released electron can combine with CO_3^- to form a CO_3^{2-} ion or with NO_3 to form a NO_3^- ion, and the colour centres will disappear. I therefore suggest that the dissociation of the hydrogen atom is the cause of bleaching in Maxixe and Maxixe-type beryl. The hydrogen atom loses its electron and the bleaching occurs when the crystals are heated above 100°C or are exposed to light.

Andersson (2008) found that some of the electrons which were released by the irradiation of Maxixe-type beryl were trapped by CO_2 molecules to form

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CO₂⁻ radicals. (This explains why the CO₂ absorption in the infrared spectrum of Krambrock *et al.* (2002) disappeared upon irradiation.) These radicals lose their electrons at a lower temperature than the hydrogen atoms and cause the initial decay of the CO₃⁻ colour centres. That is why the decay curve has two components in Maxixe-type beryl, with the slow component corresponding to the decay of the hydrogen atoms. The decay of colour in Maxixe beryl will have only one component.

NO₂ in Maxixe beryl and in a Russian beryl

The EPR signal of NO₂ has been detected in a colourless Russian beryl by Sukharzhevskii (1976). It is split into three lines by the nitrogen nucleus. These lines are of equal width and intensity when the magnetic field is oriented parallel to the crystal *c*-axis and in the spectrum they are separated by 66 Gauss, which in modern units is 6.6 milliTesla (mT). This beryl was found on the Kola peninsula in northwestern Russia (Sukharzhevskii, pers. comm., 2011). The Kola beryl has a high content of Cs ions, like the other beryls in which NO₂ has been observed.

Dr Gübelin of Lucerne kindly donated a piece from the Maxixe crystal in his collection for the EPR measurements, which were performed in 1977. I was not able to orient this irregular mm-size piece parallel to the *c*-axis, but a later extrapolation of the NO₂ signal positions observed at other angles converges to three narrow lines for the orientation parallel to the *c*-axis. This extrapolation (Andersson, 2010) was made before I was aware of the 1976 publication by Sukharzhevskii, but fits very well with his spectrum.

EPR spectra obtained with different orientations of the magnetic field give information about the orientation of the NO₂ molecule. Sukharzhevskii (1976) found that the molecular plane is perpendicular to the crystal *c*-axis and suggested that the NO₂ molecules are located between the stacks of silicate rings. Solntsev (1981) interpreted the data

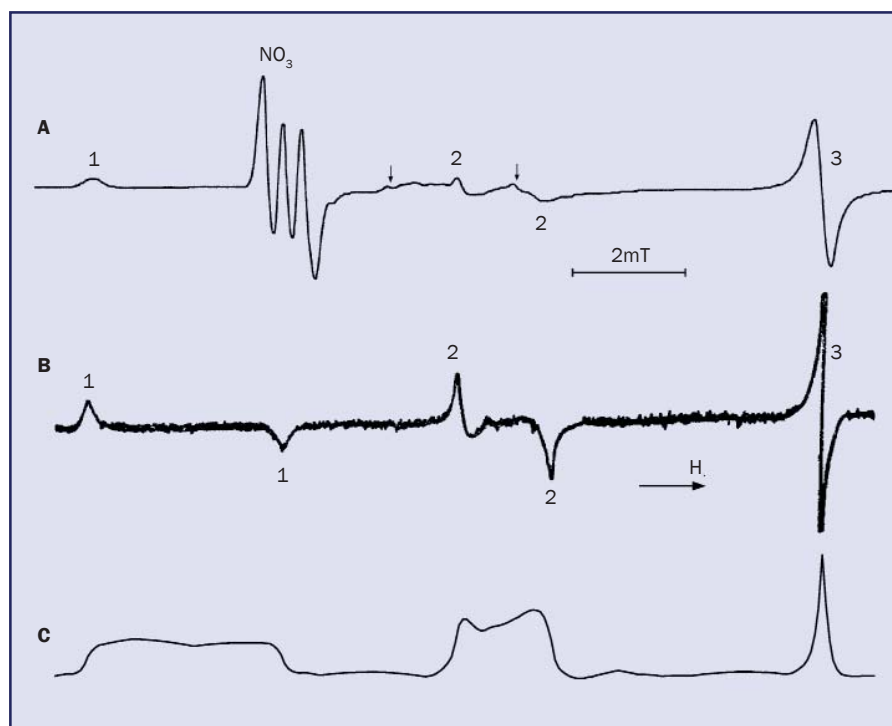


Figure 1: EPR spectra obtained at 9.2 GHz with the magnetic field *H* oriented perpendicular to the crystal *c*-axis. The strength of the field *H* is changed around the resonance field of the free electron near 330 mT. Trace A was obtained from Maxixe beryl at -180 °C and trace B from the Russian beryl at -196 °C. Trace C is the integral of the spectrum in trace B. Further explanations are given in the text.

differently and located the NO₂ molecules in the beryl channel, at the same position as the NO₃ molecules. He suggested that they are oriented in six equivalent positions in the hexagonal symmetry. Andersson (2010) found that the NO₂ molecules in Maxixe beryl are evenly distributed over all possible orientations in the plane perpendicular to the crystal *c*-axis.

The EPR spectra with the magnetic field oriented perpendicular to the crystal *c*-axis are shown for Maxixe beryl in trace A and for the Russian beryl in trace B of *Figure 1*. For technical reasons the EPR signal is recorded as the derivative of the absorption. An integration of trace B shows the three absorption lines in trace C of *Figure 1*. The two low field lines have been broadened. (Because of the background noise in trace B, the integral is not completely accurate: the areas beneath each of the three absorption lines should be equal.)

It can be seen that the intensity is evenly distributed over the range of the absorption for each of the two low field lines in trace C. If the NO₂ molecules had only six different orientations as suggested by Solntsev (1981), the low field lines should have consisted of a few separate absorptions. The absorption in trace C shows that there is an even distribution of NO₂ orientations over all angles in the Kola beryl, as there is in the Maxixe beryl.

The end points of the distributed absorptions appear clearly in the derivative spectrum in trace B and are marked with 1 and 2 for the two low field lines. These signals are also present in trace A from the Maxixe beryl. In this spectrum line 1 is partly overlapped by the signal from NO₃, which has a much smaller splitting of 0.5 mT. The EPR signal of the hydrogen atom is outside the range of *Figure 1* because the hydrogen nucleus splits the signal into two lines 50 mT apart. The EPR signal from NO₂ can

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only be observed at temperatures below $-140\text{ }^{\circ}\text{C}$ and is still somewhat broadened at $-180\text{ }^{\circ}\text{C}$. The derivative peaks are therefore not so sharp in trace A as in trace B which was obtained at $-196\text{ }^{\circ}\text{C}$.

Andersson (2010) has shown that it is a coincidence that line 3 has the same narrow shape as in the spectrum with the magnetic field parallel to the *c*-axis and that the spread of line 1 is twice as large as that of line 2. In the spectrum from an EPR spectrometer operating at another microwave frequency line 3 would also be broadened.

Discussion

Reports about NO_2 and NO_3 impurities in other beryls are rare and their concentrations have been so small that no colour has been observed. The EPR spectrum from the 1973 Maxixe-type beryl contains very small signals from NO_2 (Andersson, 2010) and NO_3 (Andersson, 1979). Solntsev (1981) reported EPR parameters for NO_2 and NO_3 in natural beryl and in synthetic hydrothermal beryl, but does not mention a blue colour or the origin of his samples. Krambrock *et al.* (2002) detected EPR signals from CO_3^- and NO_3 in natural pink beryl from Minas Gerais in Brazil. It is strange that CO_3^- is present in the unirradiated crystal and that a signal identified as NO_2 was observed only after irradiation. In a later publication, Pinheiro *et al.* (2007) reported that only the NO_3 signal was present in the natural crystal while the CO_3^- signal appeared after irradiation. The intensity of the NO_3 signal remained about the same before and after the irradiation.

An interpretation of the observations by Pinheiro *et al.* (2007) is that the natural crystal contained CO_3^{2-} and an amount of NO_3 which was not enough to give the crystal a colour. The irradiation created enough CO_3^- to colour the crystal blue but no additional NO_3 . If the natural crystal had contained NO_3^- , the irradiation should have created additional NO_3 .

Two of the possible processes for creation of the colour centre in Maxixe beryl involve NO_3^- ions and irradiation. The irradiation need not have been

artificial, but could have come from natural sources. Irradiation also creates CH_3 from CH_4 molecules in the beryl channel and the EPR signal from CH_3 can easily be detected in the spectrum from the artificially irradiated Maxixe-type beryl (Andersson, 2008). A much smaller CH_3 signal is detected in the Maxixe beryl and is indicated by arrows in trace A of *Figure 1*. Although natural radiation at the Maxixe locality may have created such a small signal, it was probably not sufficiently intense to have caused the much stronger NO_3 signal. (An alternative, but unlikely, interpretation is that the natural radiation was very strong and that the CH_4 content in Maxixe beryl was very small.) This supports the assumption that NO_3 was created by a different process and not by irradiation of NO_3^- .

The most likely process involves a combination of H_2O and NO_2 without the influence of radiation. The NO_2 molecules could have been trapped in the beryl crystals during their formation and some of these impurities have been transformed into NO_3 over geological time. This could have happened in both the Maxixe beryl and the Russian beryl. The NO_3 colour centres in the Kola beryl may then have been converted into NO_3^- by catching the electrons from the decay of the hydrogen atoms when the crystal was exposed to daylight or was heated above $100\text{ }^{\circ}\text{C}$ in recent geological time. Sukharzhevskii (1976) mentions that a zone of the crystal is weakly blue, which may indicate that some NO_3 remains.

The rest of the original NO_2 molecules are not influenced by heat or light and their EPR signal remains the same in both Maxixe and Kola beryl. The signals from the hydrogen atoms and NO_3 molecules in Maxixe beryl disappear when the crystal is bleached. The colour centres are then not converted back to NO_2 but are transformed to NO_3^- ions.

Nassau *et al.* (1976) found that the colour of bleached Maxixe beryl could be restored by irradiation with neutrons or γ -rays. This would be the case if the irradiation removes the electron from NO_3^- , which recreates the NO_3 colour centre.

Irradiation is therefore needed to restore the colour centre in Maxixe beryl, but not for its initial creation. Andersson (2008) showed that the colour of Maxixe-type beryl can be restored by UV irradiation. If this is the case also for Maxixe beryl, it may be possible that the Kola beryl could display the same deep blue colour as Maxixe beryl without the discolouring caused by more intense irradiation (Nassau *et al.*, 1976). This possibility should be borne in mind if such stones should appear in the gemstone market. Collectors and dealers should be aware that such a blue beryl would lose its colour upon extended exposure to daylight.

Conclusion

Considerable amounts of NO_2 impurities have been found in only two beryl crystals, the Kola beryl and the Maxixe beryl. The EPR spectrum of the colourless Kola beryl contains only the NO_2 signal, while that of the Maxixe beryl also contains NO_3 and hydrogen signals. The latter two signals disappear when the Maxixe beryl is bleached. The Kola beryl may therefore be a bleached Maxixe beryl and should turn blue when it is irradiated.

A definite classification of the Kola beryl as a Maxixe beryl could only be made if the NO_3 colour centre is detected after irradiation of a crystal from the same location as the beryl which was investigated in 1976.

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