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Abstract

Full Text

PHYSICS

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ON THE BLUE COLORATION OF APATITES

(Presented by Academician I. V. Belov on 8 VII 1959)

The nature of the coloration of blue apatites is a subject of discussion. Earlier, their blue color was explained by inclusions of vivianite, the presence of organic matter, etc. However, Hintze ⁽¹⁾, relying on Dolter' s data, asserted that such inclusions cannot explain the color of apatite. Dolter ⁽²⁾ and others, studying the influence of α -, β -, and γ -rays on the coloration of crystals, established that blue apatite, heated to 500°, becomes colorless, and after irradiation with cathode rays restores its original color.

Dolter did not explain the cause of this phenomenon. He noted, however, that bodies which exhibit various colors have different chemical coloring agents; the latter, in his opinion, undergo chemical change under the influence of irradiation, heating, etc. At the same time he also suggested that a change in coloration may in some cases be explained by physical changes, for example by molecular rearrangement, etc.

As a result of numerous chemical analyses it became known that manganese-bearing apatites have different colors: light blue, blue, bluish-green, violet, and pink. Therefore the cause of the coloration began to be sought in the features of the chemical composition of apatites. Thus, Quensel ⁽³⁾, studying the blue apatites of Varuträsk, isolated the so-called manganfälderites (oxyapatites), because the data of chemical analyses indicated in them a deficiency of monovalent anions. Quensel, in agreement with Rodgers ⁽⁴⁾, explains the latter by replacement of F_2 by O. Wickman ⁽⁵⁾, analyzing Quensel' s data and relying on the experiments of Blix, who tried to establish Mn in apatites in a higher oxidation state than Mn^{2+} , came to the conclusion that in apatites manganese is present only as Mn^{2+} . Z. V. Vasil'eva ⁽⁶⁾, proceeding from the assumption that in the Mn-bearing apatites she obtained no other chromophores (Fe, Cr, Cu, etc.) were detected, proposed that the coloration of apatites depends exclusively on the content of manganese entering them in various degrees of oxidation. Studying the curves of optical absorption spectra, she came to the conclusion that the blue color of apatites is due to Mn^{3+} .

Apatite is an anhydrous phosphate of the type $M_5(PO_4)_3X$, where M is represented chiefly by Ca^{2+} , sometimes isomorphously replaced by Na^+ , Mg^{2+} , Ce^{3+} , Mn^{2+} , etc.; the additional anions X are F^- , Cl^- , $(OH)^-$, O^{2-} , $(CO_3)^{2-}$. It crystallizes in the dipyramidal class of the hexagonal system; space group $P6_3/m$. In the unit cell the calcium ions occupy two positions. Some of them are in nine-

fold coordination with respect to oxygen and are located on threefold rotation axes in such a way that the axis of the coordination polyhedron coincides with the c -axis of the crystal. The other Ca^{2+} ions are in sixfold coordination and are located near the halogens; in this case the axes of the deformed octahedron do not coincide with the c -axis of the crystal (^{7,8}).

In the literature (^{3-5,9,10}) there are repeated indications that, in chemical analyses of apatites, a deficiency of halogens is often found in comparison with the theoretical formula. This circumstance is explained in different ways: by the presence of Na (¹⁰), by substitution of halogens by oxygen (^{3,4}), and sometimes this deficiency is attributed to the unreliability of chemical analyses (^{6,11}).

In the present work the results of an analysis of the electron paramagnetic resonance (E.P.R.) spectrum in single crystals of apatite are presented. Study of the spectrum makes it possible to assert that the blue color of apatites is due to color centers of the F type. Colorless and pale-pink specimens of manganese apatites exhibit an effect due to Mn^{2+} . Interpretation of the observed E.P.R. spectrum makes it possible to conclude that the fine-structure constant D is approximately 4 times greater in magnitude than the hyperfine-structure constants. $A \approx B = 95$ oersted. The indicated values of the constants A and B show that the bond of the Mn^{2+} ion with its surroundings is predominantly ionic. From comparison of the intensities of the absorption lines it follows that Mn^{2+} more readily replaces Ca^{2+} that is in ninefold coordination. Replacement of Ca^{2+} atoms that are in sixfold coordination occurs with greater difficulty.

Analysis of the E.P.R. spectrum of blue apatites from the Slyudyanka deposits shows that the concentration of Mn^{2+} in them is considerably smaller than in colorless Mn-apatite. Along with weak lines that are due to Mn^{2+} ions, an intense line (we shall call it the principal line) of width ~ 10 oersted ($g_{\parallel} = 2.003 \pm 0.001$ and $g_{\perp} = 2.050 \pm 0.001$) with six satellites was observed in the blue apatites. If the constant magnetic field is parallel to the c axis of the crystal, then the satellites are arranged symmetrically with respect to the principal line.

Heating the blue apatites in air to a temperature of $\sim 500^{\circ}$ leads to their decoloration and to the disappearance of the principal line with satellites (while the intensity of the lines due to Mn^{2+} does not change). Irradiation of crystals decolorized by heating with β - and γ -rays leads to the appearance of a pale-blue coloration, and at the same time of the principal absorption line with satellites. From this fact it may be concluded that the coloration of the crystals is due to a magnetic center that produces the E.P.R. effect. The dependence of the positions of the E.P.R. lines on the direction of the constant magnetic field relative to the c axis of the crystal indicates that the environment of the magnetic centers has axial symmetry, the axis of which coincides with the c axis of the crystal.

It was noted above that blue apatites display a deficiency of halogens. We suppose that an electron is localized in a halogen vacancy and is responsible for the E.P.R. effect. Halogen atoms in apatite are situated along the c axis of

the crystal in the environment of three Ca^{2+} atoms located at the vertices of a regular triangle. Such an arrangement of an F -center in the apatite lattice completely explains the symmetry properties of the observed spectrum. The interaction of the F -center with the magnetic moments of the nuclei of the surrounding atoms leads to the appearance of satellites.

All that has been set forth above makes it possible to conclude that the blue color of apatites is due to the localization of electrons in halide vacancies. The reason for the formation of F -centers in apatites is not yet clear. It may be assumed that it lies in the natural radioactive decay of elements that are constituents of the rocks enclosing the apatites and of accompanying minerals.

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