

Color centers in sodalite

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Abstract

Samples of natural sodalite subjected to various types of radiation and heat treatments have been studied by the techniques of electron spin resonance, nuclear magnetic resonance, optical absorption spectroscopy, ionic thermal currents and electrical conductivity. Several color centers were detected and characterized. One of them attributed to interstitial oxygen near aluminum or silicon ions is detected by the electron spin resonance and optical measurements. The variable temperature data exhibit a rapid decay process followed by a slow decay, and these two processes are believed to arise from the presence of two types of interstitial oxygen sites. Two groups of thirteen line hyperfine patterns were observed which depend on the thermal treatment of the sample before irradiation. One group has a hyperfine coupling constant of 3.5 G and the other, with a coupling constant of 32.0 G is attributed to an unpaired electron at the chlorine vacancy site. We have also observed two bands of dielectric relaxation at 20 and 50 K by means of ionic thermal currents and we report the temperature dependence of the DC electric conductivity.

Introduction

Sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$) is an aluminosilicate which belongs to the feldspathoid group of the tectosilicate minerals. The crystal structure arises from AlO_4 and SiO_4 tetrahedra which form cells within which Cl^- ions are centered in Na^+ tetrahedra. The overall structure is cubic with $a = 8.91\text{\AA}$ and a bimolecular unit cell.

A variety of natural sodalite called hackmanite and some synthetic sodalites exhibit reversible photochromism. They are colored by ultraviolet light in the wavelength range from 225 to 480 nm and are bleached by exposure to visible radiation from 480 to 750 nm. A number of experimental techniques have been employed to study this photochromism, such as optical and luminescence spectroscopy, electron spin resonance, and dielectric relaxation.

Experiments have been carried on natural and selectively doped synthetic samples over a range of temperatures and after exposure to heat treatments and radiation with visible light, ultraviolet light, electrons and X-rays. Various

workers used the resulting data to propose models to explain the photochromism. Medved (1954) provided an energy band model, and Kirk (1955) associated the optical properties with the presence of sulphur as an impurity. Ballentyne and Bye (1970) suggested that oxygen plays a dominant role. Van Den Brom et al. (1974) assumed that Al^{3+} ions in Si^{4+} sites charge compensated by Na^+ ions form electric dipoles which are reversibly oxidized or reduced. Hassib et al. (1977) attributed the coloration to sodium coagulations and chlorine ion centers. (see also, Annersten and Hassip, 1979; Paulin, 1979).

Hodgson et al., (1967) used ESR hyperfine data to conclude that when the ion S_2^- is reduced to $\text{S}_2^=$ it produces the photochromism, a mechanism supported by Povarennykh et al. (1971) in their work with the berylliosilicate tugtupite. This same group (Povarennykh et al., 1970) found that in ussingite, an alteration of sodalite, electron transfer from SO_2^- to Na^+ to produce the center SO_2^- is responsible for the color, as in the case of cancrinites (Novozhilov et al., 1966). McLaughlan and Marshall (1970a, b) found a correlation between the optical absorption and lattice spacing for a series of synthetic sodalites, but the ^{23}Na hyperfine

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coupling constant did not correlate with these factors. Accorsi et al., (1970) found that natural solalites exhibited more complex ESR spectra than synthetic specimens.

In the present work we have studied natural sodalites subjected to various types of radiation and heat treatments using the techniques of electron spin resonance (ESR), nuclear magnetic resonance (NMR), ionic thermal currents (ITC), optical absorption and electrical conductivity. A model for the color center is proposed.

Theory

Electron spin resonance

The concentration of paramagnetic centers C is given by

$$C \propto I(\Delta H_{pp})^2 \tag{1}$$

where I is the amplitude of the line and ΔH_{pp} the peak to peak line width. The Hamiltonian H that applies to the centers with electronic spin $S = \frac{1}{2}$ has an isotropic g factor and an isotropic hyperfine coupling constant A. In some cases a superhyperfine term $BS \cdot \Sigma I'$ appears, to give (Poole and Farach, 1972)

$$H = g\beta H \cdot S + AS \cdot I + BS \cdot \Sigma I' \tag{2}$$

where β is the Bohr magneton, H is the external magnetic field, I is the nuclear spin of the center and I' is the nuclear spin of the neighbors.

Ionic thermal current

When an electric field E_p is applied to a dielectric sample at a temperature T_p it polarizes the dielectric. If the sample is cooled in the presence of an electric field and heated at zero field, at a constant rate $b = dT/dt$, then, a current I(T) is produced which depends upon the temperature in accordance with the following expression

$$I(T) = \frac{\alpha N p^2 E_p}{3k T_p \tau_0} \cdot \exp\left(-\frac{\Delta U}{k_B T}\right) \cdot \exp\left[-\int_0^T \left(\frac{\exp\left(-\frac{\Delta U}{k_B T'}\right)}{b \tau_0}\right) dT'\right] \tag{3}$$

where α is a geometrical factor, N is the concentration of dipoles, p is the electric dipole moment, ΔU is the activation energy and $k_0 = 1/\tau_0$ is the attempt frequency. With the aid of equation (3) it is possible to obtain ΔU and τ_0 from the experimentally measured temperature dependence of I(T) (Bucci et al., 1966).

Electric conductivity

The thermal diffusion of ions or vacancies depends on an activation energy $\Delta U'$ related with the diffusion coefficient D through the equation

$$D = D_0 \exp(-\Delta U'/k_B T) \tag{4}$$

where D_0 is a constant, and the conductivity $\sigma(T)$ is given by

$$\sigma(T) = \frac{nq^2 D_0}{k_B T} \exp(-\Delta U'/k_B T) \tag{5}$$

where q is the charge and n is the charge carrier density. This equation is valid in the low temperature region; for high temperatures there is an extra factor

$$\sigma(T) = \frac{nq^2 D_0}{k_B T} \exp\left(-\frac{\Delta U' + \frac{1}{2}\Delta U_p}{k_B T}\right) \tag{6}$$

where ΔU_p is the energy of formation of a vacancy pair.

Optical absorption

Near infrared, visible and near ultraviolet spectroscopy, covering the range from 2500 to 200 nm, is used to measure transitions between the electronic energy levels of atoms and color centers in insulating solids. Crystal field effects play a dominant role in producing the energy level splittings observed in the visible region.

Nuclear magnetic resonance

The resonance frequency ν of a nucleus is proportional to the applied magnetic field H in accordance with the expression

$$\nu = (\gamma/2\pi)H \tag{7}$$

where γ is the gyromagnetic ratio.

Experimental methods

The present work was carried out with natural samples having a deep blue color which were obtained from Itabuna in the state of Bahia, Brazil. A Laue X-ray diffraction examination produced discrete but somewhat diffuse points suggesting that the sample was an aggregate or microcrystals with a preferential direction of orientation. Atomic absorption and gravimetric analysis provided the composition 33.2% Al_2O_3 , 37.0% SiO_2 , 20.6% Na_2O , 0.10% K_2O , 0.22% MgO , 0.12% CaO and 0.09% Fe_2O_3 with most of the remainder (8.7%) due to chlorine. X-ray fluorescence and a microprobe indicated the presence of traces of copper, and the latter technique detected chlorine.

The samples were cut into forms suitable for the various experiments, washed with carbon tetrachloride and vacuum dried at about 373 K. The ESR samples had the appropriate dimensions $3 \times 5 \times 7$ mm and those prepared for the other experimental measurements were pressed discs polished with alumina.

Heat treatments were carried out in an electric furnace. To study radiation damage effects the samples were irradiated with X-rays produced by a tungsten target with an acceleration potential of 90 kV and a filament current of 10 mA. Typical radiation times were 5 minutes. It was found that 2 MeV electrons from a linear accelerator form color centers which produce the same ESR spectra as X-rays, on the other hand, we found that UV irradiation does not produce centers.

ESR measurements were carried out with an X-band spectrometer which operates in either homodyne or superheterodyne modes. It has a Varian twelve inch electromagnet, a V-58 klystron with a power output of 600 mW and a V-4535 cylindrical cavity with a Q of about 20,000. A cryostat constructed using the design of Van der Weid (1976) was employed for carrying out measurements down to liquid nitrogen temperature, and the liquid helium studies were made with a Janis Model 1406 cryostat and a home-made cavity with a Q of about 2,000. This latter equipment was used for the spin lattice relaxation time measurements which also made use of a Microwave Associates model 8349-1 switch and a multichannel analyser. Some additional spectra were recorded on an E-line Q band spectrometer.

The ionic thermal current measurements were made using a Keithley Model 615 digital electrometer, a Hewlett Packard 6516 DC power supply, a Rikadenki B261 dual channel recorder, a cryostat and a temperature measuring device. Variable temperature measurements were made in the ranges 10 to 70 K and 77 to 300 K, using respectively a platinum resistance thermometer and a thermocouple to monitor the temperature. Indium electrodes were pressed against the sample by a spring in a sandwich type arrangement.

The apparatus for the DC electrical conductivity measurements was assembled from a Keithley model 610C electrometer, a Hewlett Packard 6102A power supply, and a dual channel ECB recorder, model RB102. Temperatures were monitored with an iron constantan thermocouple, and the samples were pressed discs 0.5 mm thick.

The optical absorption studies were carried out with a Cary-17 spectrophotometer. A Janis DT 1412 cryostat was employed for liquid helium measurements. Infrared spectra were recorded with a Perkin Elmer Model 180 spectrophotometer.

The NMR spectra were obtained for the nuclei ^{27}Al and ^{23}Na at 1.5 K, 4.2 K, 77 K and room temperature. The instrument used was a Robinson circuit with an rf oscillator in a band from 2 to 30 MHz. The magnet, lock-in detector, recorder system, etc. were those used in the ESR equipment.

Results

Electron spin resonance of unbleached samples

The room temperature spectrum of a natural sodalite sample consisted of an intense lorentzian singlet 12 G wide with $g = 2.011$, called line A, and a weak shoulder, called line B, on the high field side. A similar spectrum is obtained at both liquid nitrogen and liquid helium temperatures except that at these temperatures the width of line A has decreased to 7 G. The integrated area of line A, estimated from the amplitude times the square of the linewidth, was found to vary inversely with temperature corresponding to a Curie Law behavior. Heating the sample to 723 K bleaches the color and causes line A to disappear and to be replaced by line B, a weaker isotropic line of width 7 G and g factor 2.006. Heating for several hours at 1173 K does not cause this line to disappear.

To determine the kinetics of the reaction the intensity of the line was monitored as it disappeared for a series of temperatures in the range from 573 to 683 K, and a typical plot of the logarithm of the intensity versus the time is shown in Figure 1. The experimental data points plotted on Figure 1 fit the sum of the two straight lines shown on the figure, namely curve II corresponding to an initial rapid decay and curve I associated with a subsequent slower decay. The linearity of the curves suggests that the decay process is first order corresponding to the expression

$$N(t) = N_0 \exp(-kt) \quad (8)$$

where $N(t)$ is the number of paramagnetic centers contributing to the line and k is the rate constant. In this case there are two rate constants, k_I for the initial fast decay and k_{II} for the subsequent slow decay process. The slopes of the two straight lines on Figure 1 provide the numerical values of the two respective rate constants at the temperature of 607 K where the data were obtained.

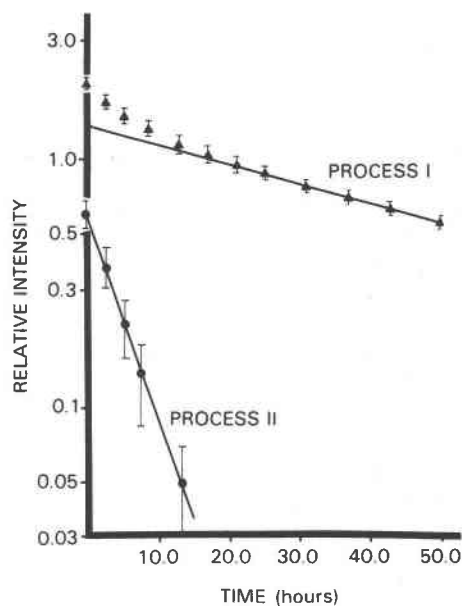


Fig. 1. Dependence of the logarithm of the intensity of ESR line A on the time. The line through the data points (Δ) corresponds to process I. The difference between this line and the data points provides the points (\cdot) of process II.

To ascertain the activation energies ΔU^{\ddagger} and the frequency factors k_0 for these two decay processes, the rate constants given by the Arrhenius equation

$$k = k_0 \exp(-\Delta U^{\ddagger}/k_B T) \quad (9)$$

were determined for a series of temperatures in the range from 573 to 683 K, and the results are plotted on Figure 2 which gives $\log k$ versus $1/T$. A least squares fit to the slopes of those curves provided the activation energies ΔU^{\ddagger} and their intercepts give the frequency factors k_0 listed in Table 1. This table also gives the time $t_{1/2}$.

$$t_{1/2} = \ln 2/k \quad (10)$$

required for half of the paramagnetic centers to disappear at 300 K.

Electron spin resonance of bleached and irradiated samples

When a sample of natural sodalite is maintained at 723 K for one hour it loses its blue color and becomes bleached. Exposure to a flux of X-rays for five minutes restores the original color. Unless otherwise stated, all irradiated samples received a five minute X-ray dose at room temperature.

The irradiated samples produced a spectrum which was the superposition of three spectra denoted line C, line D, and lines E with the following characteristics:

(1) line C is an intense isotropic singlet with the g factor of 2.011 and a peak to peak line width $\Delta H_{pp} = 12.0$ G. The integrated area of the line obeys the Curie Law in the temperature interval from 150 to 423 K,

(2) line D is an isotropic singlet of width 18 G and g factor 2.001, and

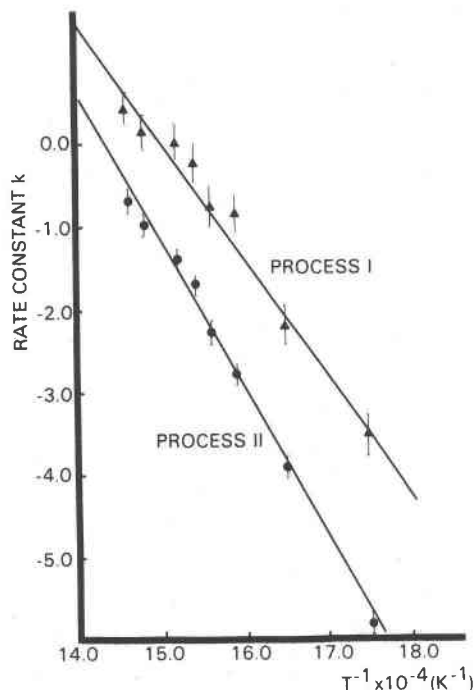


Fig. 2. Dependence of the logarithm of the rate constant *k* on the reciprocal temperature for the two processes of ESR line A shown on Fig. 1.

(3) lines E constitute a hyperfine multiplet of thirteen lines superimposed on the line D with *g* = 2.001 and separations of 3.5 G at x-band. The Q band spectrum shows the hyperfine multiplet separated from the main sharp line C.

The line widths of the hyperfine components vary between 1.0 G for the most intense ones in the center and 2.0 G for the less intense ones at the extremities of the spectrum. There was a pronounced angular variation in the hyperfine intensities with the *g*-factor, the separations and the widths of the lines remaining constant.

Table 1. Activation energies ΔU , attempt frequencies k_0 and half times $t_{1/2}$ at 300°C for various types of measurements

System Measured	ΔU , eV	k_0, s^{-1}	$t_{1/2}$ at 300K, yr
ESR line A Process II	1.22	$\sim 10^{-6}$	10^7
ESR line C Process II	1.29	10^{-7}	10^7
Optical Band 645 nm	1.3	10^{-7}	10^7
ITC Band at 20 K	0.03	10^{-6}	-
Elect. Cond. Process I	0.02	-	-
ESR line A Process I	1.56	10^{-8}	10^{10}
ESR line C Process I	1.50	10^{-8}	10^{10}
Optical Band 600 nm	1.6	10^{-9}	10^{10}
ITC Band at 49 K	0.12	10^{-10}	-
Elect. Cond. Process II	0.34	-	-
ESR line E	1.00	10^{-9}	1

When these same samples with the room temperature irradiation were examined at liquid nitrogen temperature the width of line C decreased to 7.0 G and the D line narrowed slightly. The hyperfine multiplet E did not appear since the component lines had broadened beyond 3.5 G, became extremely weak by 120 K, and disappeared before reaching 77 K. When the sample is irradiated for much longer times, line D becomes quite intense and the E multiplet disappears.

The temperature dependence of the decay of line C was studied in the range from 609 to 693 K and that of lines E in the range from 393 to 428 K to determine the kinetics of the processes. The samples were cooled to room temperature to record the spectra and then returned to the oven to continue the heating. It was found that line C decayed with two processes as shown on Figure 3, while only one process was present for the line group E. Equations (1) and (8) to (10) were employed in the manner described above to determine the activation energies, frequency factors and half time decay constants presented on Table 1 for the C and E lines.

Sodalite samples bleached at 873 K and then irradiated for five minutes acquired a blue-rose color that differed from the color acquired after bleaching at 723 K. The ESR spectrum contained line C with *g* = 2.011 and $\Delta H_{pp} = 7.0$ G, line D and a new 13 component hyperfine multiplet with *g* = 2.001 and line separation 32G which we call lines F.

When the sample is heated at 873 K for a short period of time, such as ten minutes, both E and F sets of lines appear in the ESR spectrum. A more prolonged heat treatment, in excess of an hour, at this temperature removes the E lines and causes them to be replaced by the F spectrum. The

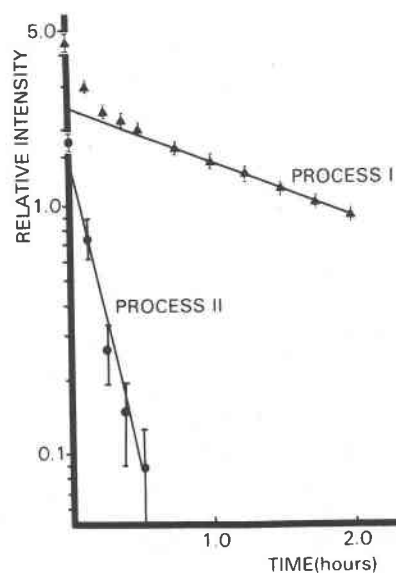


Fig. 3. Dependence of the logarithm of the intensity of ESR line C on the time. The line through the data prints (Δ) corresponds to process I. The difference between this line and the data provides the points (\cdot) of process II.

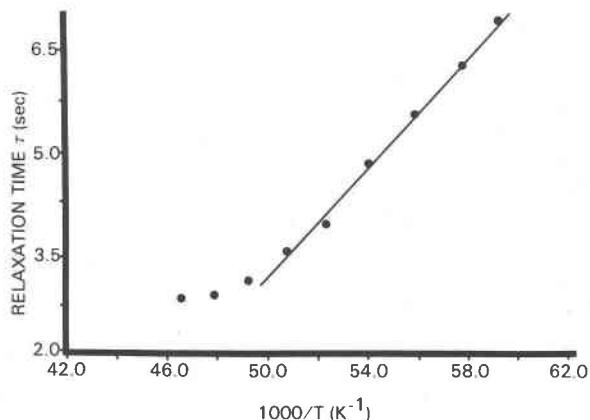


Fig. 4. Dependence of the logarithm of the relaxation time τ on the reciprocal temperature for the ITC band at 19.9 K.

relaxation time was measured for lines A and C by the technique of pulse and recovery. The results show that τ in both cases is of the order or less than $1 \mu\text{s}$.

Ionic thermal current results

Ionic thermal current measurements were made from 10 to 70 K and from 77 to 300 K. Five bands were observed in these ranges, two low temperature ones centered at 19.9 and 49.3 K two overlapping bands at 156 and 176 K and a fifth, larger one at 266 K. Each will be discussed in turn.

A computer program was employed to calculate, using equation (3), the relaxation times and the activation energies for the two lowest temperature bands, and the results are presented on Table 1. Figures 4 and 5 provide graphs of the logarithm of the relaxation time versus the reciprocal temperature for those two bands. The data on these graphs fit straight lines over much of their range, indicative of a thermal activation process. When a natural blue sodalite is bleached by heating for about one hour at 723 K the integrated areas of the two low temperature ITC bands increase by a factor of about 1.8. Exposure to X-irradiation causes these two bands to decrease with time in the manner

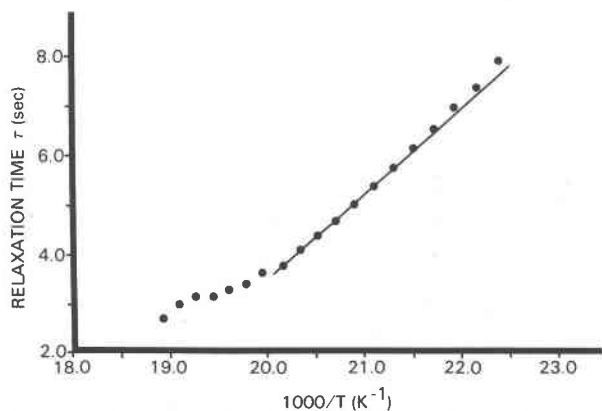


Fig. 5. Dependence of the logarithm of the relaxation time τ on the reciprocal temperature for the ITC band at 49.3 K.

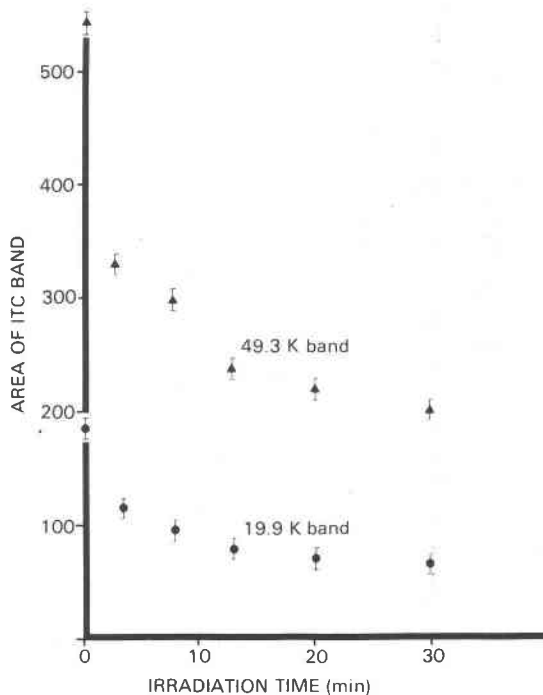


Fig. 6. Decrease in the area of the ITC bands with the time of exposure to X irradiation.

illustrated on Figure 6. When the sample is submitted to a heat treatment at 473 K for 200 hours the areas of these two bands increase appreciably, and the sample becomes insensitive to a two hour heat treatment at 723 K. This band disappears if the sample is heated at 873 K.

The three higher temperature ITC bands were insensitive both to heat treatments at 723 K and to exposure to X-irradiation. Nevertheless their high polarizability suggested that measurements be made of the electrical conductivity, and the results of these measurements will be presented in the next section.

Electrical conductivity results

DC electrical conductivity measurements were made between liquid nitrogen temperature and 773 K on natural, bleached and irradiated sodalite. The values of the electrical conductivity $\sigma(T)$ were calculated using Ohm's law

$$\sigma(T) = \frac{I(T)d}{V_0 A} \quad (11)$$

where $d \sim 0.5 \text{ mm}$ is the sample thickness, $A \sim 0.9 \text{ mm}^2$ is the surface area of the electrodes, V_0 is the applied voltage and $I(T)$ is the temperature dependent current. This law was found to be valid in the temperature range from 291 K to 743 K for applied voltages between 2 and 35 V, and the value of $V_0 = 20 \text{ V}$ was selected for carrying out the DC conductivity measurements. To evaluate the activation energy $\Delta U'$, from equation (6), the logarithm of the product $\sigma(T)T$ was plotted against $1/T$ and the results are presented on Figure 7. We see from the figure that there are two

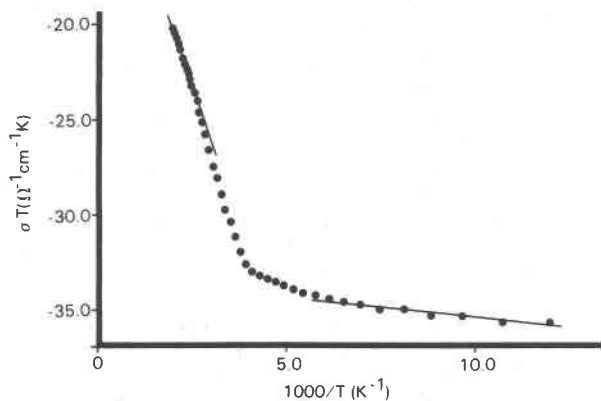


Fig. 7. Dependence of the logarithm of the product σT on the reciprocal temperature.

regions indicative of two processes I, and II with distinct activation energies, 0.02 eV, and 0.34 eV respectively.

Optical results

The optical absorption spectrum of natural sodalite exhibits two overlapping bands in the visible region at 600 and 645 nm and one ultraviolet band at 205 nm. The blue color arises from the two bands in the visible. A heat treatment for one hour at 723 K bleaches the sample by removing these two bands without affecting the one in the ultraviolet range.

The kinetics of the optical decay process were studied in the same manner as the ESR decays discussed above by plotting the optical density of each line versus time for a series of temperatures, and evaluating the slope of the line

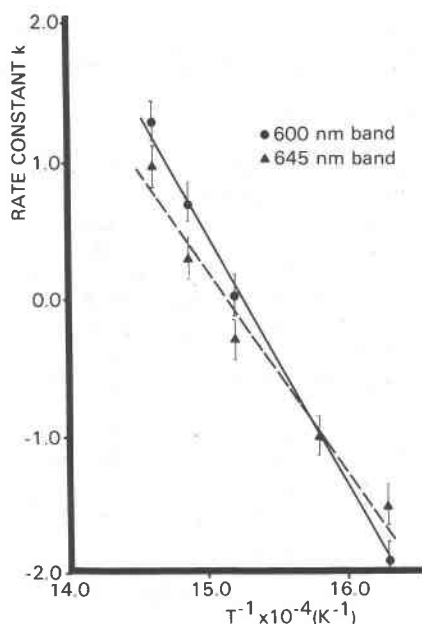


Fig. 8. Dependence of the logarithm of the rate constant for the decay of the two visible region optical bands centered at 600 nm (·) and 645 nm (Δ).

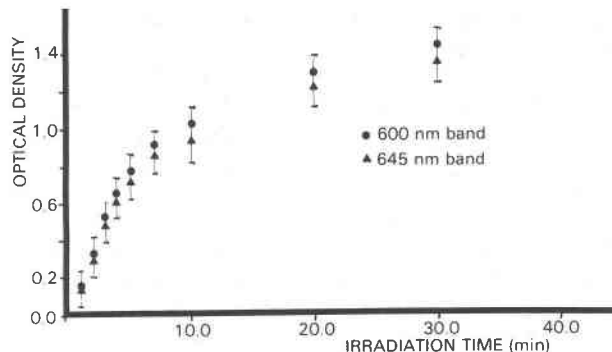


Fig. 9. Increase of the intensity of the two visible region optical absorption bands with the X-irradiation time.

at each temperature to obtain the reaction rate constant k as a function of temperature. These values were plotted versus $1/T$ on a semilogarithmic scale and the resulting least squares fit lines are presented on Figure 8. The activation energies obtained from these graphs are listed in Table 1.

Samples bleached at 723 K and then irradiated for various lengths of time produced absorption spectra, identical to those of natural samples when the dose was low, which grow with time in the manner illustrated on Figure 9. Exposure times exceeding twenty minutes produce two new absorption bands centered at 270 and 310 nm.

We noted above that samples heat treated at 873 K and then X-irradiated become blue-rose in color. The optical absorption spectra of these samples exhibit the two visible bands at 600 and 645 nm that were mentioned in the previous paragraph, and in addition the strong green band at 530 nm. Exposure of this sample to sunlight or incandescent light removes the rose line and the 530 nm band that produces it without affecting the remaining optical bands.

In the infrared region natural sodalite at room temperature exhibits infrared absorption peaks at 3540, 3040, 2050, 2025, and 1940 cm^{-1} as well as peaks characteristic of the sodalite structure in the region from 1200 to 300 cm^{-1} . Bleaching the sample for an hour at 450°C results in an additional weak line at 2340 cm^{-1} . The region between 300 and 10 cm^{-1} is currently under study in the Infrared Laboratory of the Physics Department of IFQSC-USP and will be reported later.

Nuclear magnetic resonance results

The NMR spectrum produced two lines, one 7 G wide at $\gamma = 11.262$ due to ^{23}Na nuclei, and one, 8 G wide at $\gamma = 11.094$ arising from ^{27}Al nuclei. Similar spectra were obtained at room temperature and at liquid helium temperatures, and the spectra were insensitive to heat treatments up to 723 K.

Discussion

We see from Table 1 that the activation energies ΔU , attempt frequencies k_0 and half times $t_{1/2}$ of the 600 nm

optical line, the ESR line A process I and the ESR line C process I are all quite close to each other. This permits us to conclude that all three bands have the same origin. In like manner we conclude from the data of Table 1 that the related processes II, and the optical band at 645 nm have a common origin, and we also believe that these two centers responsible for the two processes are related to each other. This means that the irradiation of a bleached sample produces the same centers that had been present in the natural sample before it was bleached. The absence of hyperfine structure suggests that this paramagnetic center is localized on one of the nuclear spin zero oxygen atoms, and the fact that the value $g = 2.011$ is larger than the free electron value of 2.0023 indicates that it is a hole center. This result is not consistent with the proposal of Hassib et al. (1977) that the color center arises from colloidal particles since the isotope ^{23}Na is 100% abundant and has the nuclear spin $I = 3/2$. Bershchov et al. (1969) proposed that the SO_4^- ion substituted for Cl^- constitutes the color center, but we did not detect any sulphur in the samples.

We propose that the centers responsible for these processes are associated with interstitial oxygen. Such a center could be formed when an X-ray knocks an electron off an oxygen ion and displaces the ion to an interstitial position in the lattice. Since the oxygens in their regular sites act as bonding bridges between adjacent aluminosilicate sites the interstitial oxygens will be closer to either Si or Al sites. Due to the difference in charge these two possibilities have different stabilities and hence they differ in their thermal activation energies. We suggest that O^- in an interstitial site with an aluminum nearest neighbor is responsible for one of the processes and O^- in an interstitial site near the silicon is responsible for the other.

The F lines with $A = 32$ G could arise from an electron localized at a Cl^- ion site in the center of a tetrahedron of Na^+ ions since this center is well known in sodalite as being responsible for the rose color of a sample bleached at 873 K and then subsequently irradiated (McLaughlan and Marshall, 1970). The E lines have too small a hyperfine interaction (3 G) to arise from this center and we have not identified it so far nor have we identified the center for the ITC bands. We are doing a more detailed analysis of these centers and we plan to report the results later. Kasai (1965) and Vadrine and Naccache (1973) observed a 13 line hyperfine pattern with $A = 32.3$ G in gamma irradiated Y-sodalite and attributed it to an electron trapped inside a tetrahedron of Na^+ ions.

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References

- Accorsi, A., Debron, G., Legrand, A. P. and Maury, R. (1970) Observation of paramagnetic centers in sodalite. *Comptes Rendus hebdomadaires des Séances de L'Academie des Sciences*, 271, 1930-1933.
- Annersten, H. and Hassib, A. (1979) Blue sodalite, *Canadian Mineralogist*, 17, 39-46.
- Ballentyne, D. E. G. and Bye, K. L. J. (1970) The nature of photochromism. In *Chlorosodalites from Optical Data*, *Journal of Physics D: Applied Physics*, 3, 1438-1443.
- Berschov, L. V., Martirosyan, V. O., Platonov, A. N. and Tatashan, A. N. (1969) EPR of the titanium (III) ion in beryls. *Izvestiya Akademii Nauk SSSR Neorganicheskie Materialy*, 5, 1780-1784 (in Russian).
- Bucci, C., Cappalletti, R., Fieschi, R., Guidi, G. and Pirola, L. (1966) Ionic thermal currents in dielectric solids, *Suppl. II Nuovo Cimento*, IV, 607.
- Hassib, A., Beckman, O. and Annersten, H. (1977) Photochromic properties of natural sodalite. *Journal of Physics D: Applied Physics*, 10, 771-777.
- Hodgson, W. G., Brinen, J. S. and Williams, E. F. (1967) Electron spin resonance investigation of photochromic sodalites. *Journal of Chemical Physics*, 47, 3719-3723.
- Kasai, P. H. (1965) Electron spin resonance studies of gamma and X-ray irradiated zeolites. *Journal of Chemical Physics*, 43, 3322-3327.
- Kirk, R. D. (1955) The luminescence and tenebrescence of natural and synthetic sodalite. *American Mineralogist*, 40, 22.
- McLaughlan, S. C. and Marshall, D. J. (1970a) Paramagnetic resonance of F-type centres in photochromic sodalites. *Physics Letters*, 32A, 343-344.
- McLaughlan, S. D. and Marshall, D. J. (1970b) Paramagnetic resonance of sulfur radicals in synthetic sodalites. *Journal of Physical Chemistry*, 74, 1359-1363.
- Medved, D. B. (1954) Hackmanite and its tenebrescent properties. *American Mineralogist*, 39, 615-629.
- Novozhilov, A. I., Samoilovich, M. I., Mikul'skaya, E. K. and Parusnikova, L. I. (1966) The Nature of the blue coloration of cancrinite crystals. *Zapiski Vsesoiuznoe Mineralogicheskoe Obshchestvo*, 95, 736-738.
- Paulin, P. E. (1979) The blue colour of sodalite. *Journal of Gemmology*, 16, 452-454.
- Poole, C. P., Jr. and Farach, H. A. (1972) *Theory of Magnetic Resonance*. Wiley-Interscience, New York.
- Povarennykh, A. S., Platonov, A. N. and Belichenko, V. P. (1970) On the colour of ussingite from the Ilimaussag (South Greenland) and Lovozero (Kolo Peninsula) alkaline intrusions. *Bulletin of Geological Society of Denmark*, 20, 20-26.
- Povarennykh, A. S., Platonov, A. N., Tarashchan, A. N. and Belichenko, V. P. (1971) The colour and luminescence of tugtupite (berylsodalite) from Ilimaussag, South Greenland. *Meddr. om Grønland*, 181, 1-12.
- Van Den Brom, W. E., Kerksen, J. and Volger, J. (1974) Electron spin resonance study of oxygen species absorbed on gamma irradiated zeolites. *Physica*, 77, 1.
- Van Der Weid, J. P. (1976) Croystat for ESR, *Revista Brasileira*, 6, 1.
- Vadrine, J. C. and Naccache, C. (1973) Electric dipole centers and color centers in natural sodalite. *Journal of Physical Chemistry*, 77, 1606.

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