Lattice-stabilized CH$_3$, C$_2$H$_5$, NO$_2$, and O$^{1-}$ radicals in feldspar with different Al-Si order

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ABSTRACT

Single crystals of feldspar with varying degrees of Al-Si order and from different petrogenetic areas were studied using electron paramagnetic resonance (EPR) spectroscopy. EPR spectra of lattice-stabilized CH$_3$, C$_2$H$_5$, and NO$_2$ free radicals could be detected in pegmatic microcline and hyalophane. Spectra of this type were observed in microcline from pegmatites and granites of the Ukrainian Shield by Matyash et al. (1981, 1982), but the hydrocarbons were interpreted as HN$_3$ and NO$_2$ as N$_2$. Methyl and ethyl radicals at M positions in the feldspar structure are formed from methane and ethane after natural or artificial irradiation.

The CH$_3$ and NO$_2$ radicals in 34 microcline and hyalophane crystals and those reported by Matyash et al. (1981, 1982) show similar eigenvalues and direction cosines of the g and T tensors. The calculated spin densities in the NO$_2$ radical for temperatures between 295 and 30 K are $c'_u = 0.092-0.096$ and $c'_e = 0.322-0.610$ on the N atom. In this temperature range the O-N-O angle varies between 129–138 and 130–140° for hyalophane and microcline, respectively.

Based on comparison of the direction cosines of the g tensor and T-T directions in the feldspar structure, five O$^{1-}$/2$^{27}$Al centers could be assigned to the bridges Al$_{410}$O$_{16}$-Al$_{11m}$, Al$_{410}$O$_{16}$-Al$_{22m}$, Al$_{410}$O$_{16}$-Al$_{22m}$, Al$_{410}$O$_{16}$-Al$_{22m}$, and Al$_{410}$O$_{16}$-Al$_{22m}$ (violations of the rule of Loewenstein) in different samples and are designated as a$^u$, c$_o$, d$_o$, c$_m$, and d$_m$, respectively. In albite one additional O$^{1-}$/2$^{27}$Al $\times$ 2$^{23}$Na center could be assigned to a Si$_{410}$O$_{16}$-Al$_{11m}$ bridge with two adjacent quasi-equidistant Na atoms and is designated as a$^a$. In feldspars with large M cations (M = K, Ba), independent of their degree of long-range Al-Si order, only a$^u$ and d$_m$ centers are formed, with a concentration ratio 3:1. In albite a$^u$, c$_o$, d$_o$, c$_m$, and d$_m$ centers with a concentration ratio 2:2:2:1:1 are present. After irradiation of ordered and disordered feldspars, O$^{1-}$/2$^{27}$Al centers could be created only in quasi-ordered domains of similar Al-Si order. Their total concentration is approximately the same in feldspars with large and small M cations. The short-range Al site occupancy in such domains indicated different ordering paths in feldspars with large and small M cations.

In the feldspar structure crystal defects, for example, O$^{1-}$/2$^{27}$Al centers and OH or H$_2$O may support the Al-Si exchange, whereas thermally stable Fe$^{3+}$ substituting for Al at border tetrahedra between ordered and disordered domains can act as a stabilizer. With increasing total Fe$_2$O$_3$ content the concentration of O$^{1-}$/2$^{27}$Al centers decreases, the substitution of Fe$^{3+}$ at tetrahedral positions increases, and the Al-Si exchange kinetics becomes slower.

INTRODUCTION

The type and concentration of crystal defects in natural minerals will certainly depend on the presence of specific ions in mineral-forming fluids, P, T, P$_{0}$, T, etc., and small deviations in thermodynamic relationships during crystallization. Subsequent processes such as metasomatism, metamorphism, and natural irradiation can also influence these defects; thus the real structure of a mineral reflects its geological history. Crystal defects are central to the kinetics of transport in minerals and are essential in many geochemical processes, e.g., alteration of the composition of minerals, homogenization of zoned crystals, changes in the degree of Al-Si order in aluminosilicates, etc. These crystal defects are inherently paramagnetic or become paramagnetic by natural or artificial irradiation; thus they are detectable by electron paramagnetic resonance (EPR). The study of impurity paramagnetic centers may give information about the crystallographical position (substitution at a structural site, interstitial, distribution of nonequivalent sites), valence and bonding state of trace elements, and data on more complex centers that can only be provided by other meth-
ods with some difficulty. Thus, the study of many crystalchemical, geochemical, and petrological phenomena is possible on an atomic scale.

In the past three decades 20 paramagnetic centers have been detected by EPR measurements of oriented single crystals, and their positions in the structure of natural feldspars were determined (Table 1). Their spectra can be observed between 4.2 and 295 K, showing different characteristic temperatures $T_m$, where the intensities of the EPR lines are at a maximum. $T_m$ can depend on center concentration and the degree of Al-Si order. Only the 3d impurity paramagnetic centers, Fe$^{3+}$ and Mn$^{2+}$, are bonded covalently to the diamagnetic O$^{2-}$ ligands. They are thermally stable and cannot be destroyed by heating at annihilation temperatures $T_A$ above 873 K. Thermally metastable paramagnetic centers have $T_A \leq 873$ K for various annihilation times $t_A$ above 873 K. Thermally metastable paramagnetic centers have $T_A \leq 873$ K for various annihilation times $t_A$ and can be reactivated after subsequent natural or artificial irradiation. Therefore, systematic studies of $T_A$ and concentration of these centers can recognize thermodynamic and radiologic gradients in geological profiles. These paramagnetic centers can be summarized into four main groups: cations and anions with unusual valence, BO$_n^m$ radicals, and organic radicals (Table 1).

In ordered alkali feldspars, Fe$^{3+}$ occupies the T10 position (Hochli, 1964; Marfunin and Michoulier, 1966; Marfunin et al., 1967; Gaite and Michoulier, 1970; Michoulier and Gaite, 1972; Petrov et al., 1989a). In disordered ones it is found at the T1 and T2 positions, as well as in tetrahedra of type TO$_3$OH (Petrov and Hafner, 1988). In hydrocarbon-bearing hyalophane, FeO'(OH)$_2$ centers occur after X-ray or $\gamma$ irradiation (Petrov, 1992). Three lattice positions of Fe$^{3+}$ in the structure of intermediate plagioclase are still under discussion (Marfunin and Michoulier, 1966; Marfunin et al., 1967; Gaite and Michoulier, 1970; Michoulier and Gaite, 1972; Petrov et al., 1989a). In disordered ones it is found at the T1 and T2 positions, as well as in tetrahedra of type TO$_3$OH (Petrov and Hafner, 1988). In hydrocarbon-bearing hyalophane, FeO$_2$(OH)$_2$ centers occur after X-ray or $\gamma$ irradiation (Petrov, 1992). Three lattice positions of Fe$^{3+}$ in the structure of intermediate plagioclase are still under discussion (Marfunin and Michoulier, 1966; Marfunin et al., 1967; Gaite and Michoulier, 1970; Michoulier and Gaite, 1972; Petrov et al., 1989a).

Mn$^{2+}$ was detected in oligoclase (Marfunin and Michoulier, 1966; Matyash et al., 1981), anorthite (Niebuhr et al., 1973), albite (Petrov et al., 1989a), and sanidine after heat treatment at 1323 during $t_A = 3300$ h (Petrov, unpublished data). The Ti$^{3+}$ electron center (Ti$^{3+} + e$)

### Table 1. Paramagnetic centers in alkali feldspar

<table>
<thead>
<tr>
<th>Paramagnetic center</th>
<th>Notation/site</th>
<th>Degree of Si-Al order</th>
<th>$T_m$ (K)</th>
<th>$T_A$ (K)</th>
<th>$t_A$ (h)</th>
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<td>T10</td>
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<td>&gt;3300</td>
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<tr>
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<td>T10</td>
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<td>295</td>
<td>&gt;1323</td>
<td>&gt;1300</td>
<td>g</td>
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<td>15</td>
<td>&gt;1273</td>
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<tr>
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<td>ordered + disordered</td>
<td>295</td>
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<td>&gt;3300</td>
<td>b,f,l,j</td>
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<tr>
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<td>disordered</td>
<td>295</td>
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<td>&gt;1</td>
<td>b,f,j,k</td>
</tr>
</tbody>
</table>

**Thermally stable centers:** Cations with $d^5$ electron configuration

- Fe$^{3+}$, Mn$^{2+}$
- $Fe_2^+$O$^+$, $Fe_3^+$O$^+$, $Fe_4^+$O$^+$, $Fe_5^+$O$^+$
- $Fe_6^+$O$^+$OH$^-$(OH$^+$)
- $Fe_7^+$O$^+$(OH$^+$)
- $Fe_8^+$O$^+$(OH$^+$)
- $Fe_9^+$O$^+$(OH$^+$)
- $Fe_10^+$O$^+$(OH$^+$)
- $Fe_11^+$O$^+$(OH$^+$)

**Iron oxides**

- Cations with unusual valence: $d^3$ electron configuration
- $Fe_1^+$O$^+$, $Fe_2^+$O$^+$, $Fe_3^+$O$^+$, $Fe_4^+$O$^+$
- $Fe_5^+$O$^+$, $Fe_6^+$O$^+$, $Fe_7^+$O$^+$, $Fe_8^+$O$^+$

**Organic radicals**

- $BO_2^-$
- $BO_3^-$
- $BO_4^-$
- $BO_5^-$
- $BO_6^-$
- $BO_7^-$
- $BO_8^-$

**Anions with unusual valence:** $p^5$ electron configuration ($O'^{-}/M^+$, and $O'^{-}/2M^+$, $x > 2M^+$ centers)

- $M_1^+$, $M_2^+$, $M_3^+$, $M_4^+$, $M_5^+$, $M_6^+$, $M_7^+$, $M_8^+$, $M_9^+$, $M_{10}^+$

**References**


* Interpreted as $Nh_2^+$ by authors m and n, respectively, by authors m.
† Interpreted as $Nh_2^+$ by authors f, i, o.
‡ Interpreted as $Nh_2^+$ by authors f, i, o.
Fig. 1. Projection of the crystal structure of feldspar on the (201) plane. The projections of a and b are identical. In a, the atomic positions of Na, Al, Si, and O are labeled using the notation of Megaw (1956). The T10 tetrahedra of the regular Al position in ordered feldspar are shaded.

In b, the most probable assignments of the O'-/23Al centers are marked by heavy lines. These were obtained from the $g_{e}$ eigenvectors of the mean positions of the centers, which are assumed to be about parallel to the direction of the line connecting the two effective T positions. The $g_{e}$ eigenvectors of the O'-/ (Si,M') centers are approximately parallel to the T-O direction.

Distinct O'/ (Si,M') centers, $a_{o}$, $b_{o}$, and $c_{o}$, are assigned to the bridges $Al_{T10}-O_{Al}-Al_{T10}$, $Al_{T10}-O_{Al}-Al_{T10}$, $Al_{T10}-O_{Al}-Al_{T10}$, and $Al_{T10}-O_{Al}-Al_{T10}$, respectively.

The O'/ (Si,M') × 2Na center, $a_{N}$, is assigned to a $Si_{T10}-O_{Al}-Al_{T10}$ bridge that possesses two adjacent quasi-equidistant Na atoms. The distinct O'/ (Si,M') centers, $h_{o}$, $h_{c}$, and $h_{d}$, are assigned to O' at B, C, and D, with a bivalent cation, e.g., Mg', substituted for one of the Si atoms at the two adjacent T10 and T20 or T20 and Al10 tetrahedra.

was detected in various ordered and disordered feldspars (Marfunin and Bershov, 1970; Speit and Lehmann, 1982). The [Pb-Pb]' dimeric center ([Pb-Pb]' + e) was discovered in amazinite-type microcline (Petrov et al., 1993). Distinct O' hole centers were observed in different ordered and disordered feldspars (Joffe and Yanchevskaya, 1968; Marfunin and Bershov, 1970; Speit and Lehmann, 1976, 1982; Matyash et al., 1981, 1982; Petrov et al., 1989b). They can be described by the formula

$$\text{O'} / \sum_{j=1}^{m} Y_{j} \times \sum_{z=1}^{m} Z_{z} \times \ldots \text{ and } \text{O'} / \left( \sum_{j=1}^{m} M_{j} \right)$$

(1)

where $Y_{j}$ and $Z_{j}$ are adjacent nuclei with $I > 0$, giving a hyperfine structure (HFS) and $M_{j}$ adjacent nuclei with $I = 0$, without HFS. In feldspar $Y_{i} = 27\text{Al}$, $23\text{Na}$, $107,109\text{Ag}$, $208\text{Pb}$, $Z_{i} = 23\text{Na}$, and $M = \text{unidentified cation}$, e.g., $\text{Si}^{2+}$, $\text{Mg}^{2+}$ (Petrov et al., 1989b). Centers with $Y_{i} = 27\text{Al}$, $n = 2$, (i.e., Al-O'-Al bridges) cause a violation of the principle of Loewenstein (1954). The notation $a_{i}$, $b_{o}$, $c_{o}$, etc., describes O' centers created at Al, B0, C0, etc., O positions in the feldspar structure (Fig. 1).

O' vacancies at Si tetrahedra with one captured electron (SiO$^-$ radical) are similar to the E' centers in quartz. PO$^+$ electron centers were formed by substitution of P$^+$ for Si$^{4+}$ with an O vacancy and one captured electron in the complex.

EPR spectra of the free radicals NO, CH$_3$, and C$_2$H$_4$ were observed first by Matyash et al. (1981, 1982) in pegmatitic microcline from the Ukrainian Shield, but the NO$_2$ centers were interpreted as N$_2$ at D$_m$ O positions (Si-N$_2$-Si) and the hydrocarbon centers as NH$_3$.

Natural fluids of the system C-O-H-N are important because of their geochemical significance. During crystallization, small parts of N- and hydrocarbon-bearing fluids can be trapped in the host crystal. Intracrystalline fluid inclusions of this composition have been investigated by analytical methods and Raman spectroscopy mainly in quartz, but only slightly in feldspar. However, information on the substitution of N and hydrocarbons in minerals is rare; their substitution in the structure of feldspar has not been reported. In the present study, the substitution of NO$_2$, CH$_3$, and C$_2$H$_4$ in microcline and hyalophane is discussed, and new data on the distribution of Al-O'-Al fragments in the structure of feldspars with large and small M cations are reported.

**EPR spectra of free radicals**

Generally, free radicals in minerals represent ions or segments of molecules containing one unpaired spin,
thereby trapping or losing an electron. They do not occur as isolated groups because of the existence of a free valency but are stabilized by the crystal lattice. Irradiation-induced, thermally metastable paramagnetic centers in feldspar with annihilation temperatures \( T_a \leq 873 \) K (cf. Table 1) match these criteria.

Induced, thermally metastable paramagnetic centers in feldspar are stabilized by the crystal lattice. Irradiation-induced radicals in feldspar are stabilized by the crystal lattice.

Fig. 2. Hyperfine structure patterns of methyl and ethyl radicals in feldspar.

The EPR spectrum of such a system consisting of one electron with spin \( S = \frac{1}{2} \) and \( n \) nuclei of spin \( I \), may be described by the spin Hamiltonian

\[
\mathcal{H} = \beta B g S + \sum_{i=1}^{n} S A_i I_i
\]  

where \( \beta \) is the Bohr magneton, \( S \) and \( I \) are the electron and nucleus operators, respectively, \( g \) and \( A \) are the spectroscopic splitting factor and HFS tensors, respectively, and \( B \) is the Zeeman field vector. Terms of the nuclear Zeeman energy and the nuclear quadrupole energy are omitted from Equation 2, since they are small.

In general, HFS tensor components may be written as sums:

\[ A_{ii} = A_{iso} + T_{ii} \]  

where \( A_{iso} \) is the isotropic hyperfine interaction (HFI) or Fermi contact interaction, and \( T_{ii} \) are the principal components of the traceless dipole-dipole or anisotropic interaction tensor. Consequently, the HFS data may be analyzed with the aid of the expressions

\[ A_{iso} = 8 \gamma g_0 g_e \beta_e |\Psi_e(O)|^2 |c_s|^2 \]  

and

\[ T_{ii} = \gamma g_0 g_e \beta_e (r^{-3})_{np} |c_{np}|^2 \]  

where \( s \) and \( p \) relate to the central atom orbitals, and the parameters \( c_s^2 \) and \( c_p^2 \) represent the fraction of unpaired electron spin density at the central atom \( s \) and \( p \) orbitals, respectively.

Organic radicals

For most organic free radicals, since the orbital angular momentum is quenched, and \( g \) has an almost isotropic value close to \( g_e = 2.0023 \), the value of the free electron, the difference \( g_a - g_e = A_{iso} (i = x, y, z) \) is small. Therefore, for an unambiguous identification of organic free radicals their HFS patterns are important. The number and the intensity ratio of HFS components give information about the radical structure. If the radical is observed in solution, the anisotropic contributions \( T_{ii} \) to the HFI between \( S \) and \( I \) are generally averaged to zero. Thus the HFS spectra of most organic radicals in fluid media can be interpreted simply by the third term, \( S A_i I_i \), of Equation 2. For organic paramagnetic centers examined in fixed orientations to \( B \), as in a single crystal, in which the effect of the coupling between electron spin and orbital angular momentum can be observed, anisotropy in \( g \), as well as \( A_{iso} \) and \( T_{ii} \) from Equation 3 must be taken into account. For intermediate situations, e.g., for radicals trapped in polycrystalline matrices, which occupy sites with random orientations with respect to \( B \), \( A_{iso} \) and \( T_{ii} \) components may be separated only in favorable cases. In many systems \( A_{iso} \) is much greater in magnitude than \( T_{ii} \), and so the latter cause only line broadening.

According to Equation 3 a Fermi contact interaction \( A_{iso} \) can be expected only for radicals with \( c_s^2 > 0 \). But most organic radicals are \( \pi \) radicals, with their unpaired electron localized in an orbital without an \( s \) character. The unpaired electron in the \( \text{CH}_3 \) radical occupies a \( 2p_z \) orbital in the carbon sp\(^2\) hybrid orbital. The \( 2p_z \) orbital is oriented perpendicular to the >C-H bond. Because of the \( \pi-\sigma \) spin polarization, a contact interaction between the unpaired electron and the three equivalent protons takes place. Theoretical calculations suggest that the unpaired \( 2p_z \) electron induces a negative spin density of about \( c_s^2 = -0.05 \) in the \( 1s \) orbital, corresponding to a HF coupling constant \( A_{iso} \) of \(-56\) up to \(-70\) MHz (e.g., Carrington and McLachlan, 1967). Experimental data are in good agreement with these values (Jen et al., 1968; Fessenden and Schuler, 1963; Bersohn and Baird, 1966; Ayscough, 1967; Carrington and McLachlan, 1967; Wertz and Bolton, 1972).

In general, if the unpaired electron interacts with an arbitrary number of sets of equivalent protons, the number of equivalent nuclei with spin \( I \), \( n_i \), is the number of equivalent nuclei with spin \( I \), and \( \Pi \), indicates a product over all values of \( i \). Of equivalent nuclei can be treated by considering that they interact as one nucleus with a nuclear spin equal to the sum of all the nuclear spins in the equivalent set. Thus, if there are \( n \) equivalent nuclei of spin \( I \), the HFI between \( S \) and \( I \) in the second term of Equation 2 leads to an EPR spectrum that consists of \( N_{eq} = (2n I + 1) \) lines. Their intensities are proportional to the coefficients of the binomial expansion of \((1 + x)^n\). The three equivalent protons \((I = \frac{1}{2}, 1\) natural abundance 99.988\%) of the methyl radical lead to a multiple that consists of \( N_{eq} = 4 \) lines with an intensity ratio of 1:3:3:1 (Fig. 2). The portion of the \(^{12}\text{C} \) nucleus with \( I = 0 \) is 98.9%; thus no additional HFS appears. The remaining 1.1% belongs to the \(^{13}\text{C} \) nuclei with \( I = \frac{1}{2} \), which can give an additional HFS. How-
ever, it is too weak to be observed in spectra of natural minerals.

If there exist two sets of $n_a$ and $n_b$ equivalent protons, then the maximum possible $N_{\text{HFS}}$ in the spectrum will be given by $(2n_a I_a + 1)(2n_b I_b + 1)$. For the ethyl radical with two equivalent CH$_3$ and three equivalent CH$_2$ protons ($I_a = I_b$), 12 lines with an intensity ratio of 1:2:3:1:6:3:3:6:1:3:2:1 are expected. As shown in Figure 2, the HFI with two sets of protons with different HF splittings gives spectra rich in line components. More complex HFS patterns and intensity ratios were produced by superposition of such spectra of distinct centers so that an unambiguous identification of the centers is difficult. The overlapping of ethyl and methyl spectra in feldspar is schematically shown in Figure 2.

In the usual notation the C atom holding the unpaired electron is designated as $\alpha$ carbon, and the protons bonded to it are labeled $\alpha$ protons. The C atoms bonded to the $\alpha$ carbon are designated as $\beta$ carbon atoms, and the protons bonded to the $\beta$ carbon atoms are called $\beta$ protons. In the ethyl radical CH$_2$CH$_3$, the unpaired electron is localized in the 2$\pi_a$ orbital of the $\cdots$CH$_2$ group. Analogous to the methyl radical, a negative spin density in the 1$s$ orbital of the ethylene $\alpha$ protons is induced by the $\pi$-$\alpha$ spin polarization, corresponding to $A_{\text{iso}} \approx -63$ MHz (Fessenden and Schuler, 1963; Bersohn and Baird, 1966; Ayscough, 1967; Carington and McLachlan, 1967; Wertz and Bolton, 1970). The $\beta$ methyl protons lie in a plane parallel to the axis of the 2$p_z$ orbital of the unpaired electron, perpendicular to the C-C bond. The unpaired electron is delocalized into the $\beta$ proton 1$s$ orbital by a hyperconjugative mechanism, the resulting positive spin density is $A_{\text{iso}} \approx 78$ MHz.

theory and experiment indicate that in radicals of this type the $\beta$ hydrogen nuclei have approximately isotropic HFI. However, the $\alpha$ hydrogen nuclei will also experience an anisotropic HFI of the same order of magnitude as the isotropic HFI, whereas the HF anisotropy experienced by the $\beta$ hydrogen atoms will be considerably smaller (e.g., Ayscough, 1967; Wertz and Bolton, 1972). In crystalline matrices the effect of the anisotropic HFI with the $\alpha$ hydrogen atoms will depend on the rotational freedom of the radical, e.g., the possibility of cancellation between two such $\alpha$ hydrogen atoms, local disorder around the radical site, etc. These effects can lead to increasing line width and a change in line shape. In polycrystalline matrices with a random orientation of T with respect to B, this anisotropy will produce a broadening of the lines, which may range from an obliteration of fine details of the spectrum to extreme broadening, so that the spectrum may appear as a single broad, weak (or even undetectable) line.

Inorganic radicals

As is the case for organic radicals, the values of $T_{\text{e}}$, and $N_{\text{HFS}}$ in Equations 3 and 6, respectively, can provide the major clues in the identification of most inorganic radicals. However, the appearance of HFS is not sufficient to provide a positive identification. Paramagnetic centers as N, NO$_2$, NO$^+_2$, NO$_3^-$, and NO$^+_3$, which contain a N atom, are characterized by $N_{\text{HFS}} = 3$. However, assignment to specific radicals requires a knowledge of the theoretical predictions of the structure and orbital sequence of each radical; in addition, one requires information from studies of these radicals in other host matrices. In various host matrices, NO$_3$ exhibits a $^{17}$N HFI with little anisotropy, and $A_{\text{iso}} \approx 150$ MHz. The small anisotropy arises from the fact that NO$_3$ is usually rotating around its two-fold axis, even in a solid. NO$_2$ fixed in a host crystal exhibits considerable anisotropy. The large $A_{\text{iso}}$ arises from the fact that the unpaired electron is located primarily in a nonbonding sp$^3$ orbital of N.

The NO$_2$ radical has 17 valence electrons with a ground-state electron configuration (3$s$)$^2$(4$s$)$^3$ and is predicted to have a bent structure with an O-N-O angle of about 134° (Ayscough, 1967; Atkins and Symons, 1967; Wertz and Bolton, 1970; Gimarc, 1979). Excitation of an electron from the lower 3$s$ to (3$s$)$^2$(4$s$)$^3$ makes this excited state of NO$_2$ more strongly bent (112°).

For such radicals, which have $C_{3v}$ symmetry, the unpaired electron is in the antibonding 4$a_1$ orbital, which is a mixture of $s$ and $p_\alpha$ central atom orbitals and a symmetry-adapted linear combination of O 2$s$ and 2$p$ orbitals (e.g., Carrington and McLachlan, 1967). The general form of this orbital can be represented as

$$\Psi(4a_1) = c_1\psi_1(2s) + c_2\psi_2(2p) + c_3\psi_3(2p)$$

where $\psi_1$ is the central atom orbital, $\psi_2$ is a linear combination of O 2$s$ and 2$p$ orbitals, and $c_1^2 + c_2^2 + c_3^2 = 1$.

The NO$_2$ radical the eigenvector $g_{ex}$ is perpendicular to the plane of the radical; the eigenvector $g_{ey}$ is directed along the O-O direction, and $g_{ez}$ bisects the O-N-O angle (Atkins and Symons, 1967; Carrington and McLachlan, 1967). The constants of the isotropic HFI and the components of the tensor of dipole-dipole HFI may be written as $A_{\text{iso}} = \Sigma A_{\text{HFI}}$ and $T_{\text{e}} = A_{\text{HFI}} - A_{\text{iso}}$, respectively. Spin densities ($s$ and $p$ contribution) on the N atom are defined as $c_1^2 = A_{\text{HFI}}/A_{\text{iso}}$, $c_2^2 = T_{\text{e}}/T^*$, where $A_{\text{iso}} = 1811$ MHz and $T_{\text{e}}/T^* = 55.52$ MHz are the constants of the isotropic and anisotropic HFI for a free N atom (Morton and Preston, 1978). From the calculated values of $c_1^2$ and $c_2^2$, the p to s hybridization ratio $\lambda^2 = c_2^2/c_1^2$ can be determined for which the bond angle is given by

$$\rho = 2 \cos^{-1}(\lambda^2 + 2)^{-1/2}$$

O$^{17}$ centers from Equation 1 with $Y_{\text{e}} = ^{27}$Al and $n = 2$, described in detail in Petrov et al. (1989b), can be identified by its characteristic spectrum of $N_{\text{HFS}} = 11$, exhibiting line intensities according to the approximate ratio 1:2:3:4:5:6:5:4:3:2:1. A HFS pattern of this type is due to the interaction of an unpaired electron ($S = 1/2$) with two adjacent Al nuclei ($I = 3/2$, natural abundance of $^{27}$Al 100%), which are separated from the hole center by about the same distance.

SAMPLES

The investigated crystals of hydrocarbon-bearing microcline and hyalophane (a monoclinic barium potassium
Table 2. Microprobe analyses of microcline and hyalophane

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Note: microprobe analyses by J.M. Claude, Université de Nancy. Analyses are given in weight percentages.

Chemical analyses of microcline and hyalophane are given in Table 2. No phases other than sodium feldspar and potassium feldspar were revealed by X-ray phase analyses of microcline. The sanidine samples (Orₓ=0.82) were fragments of megacrystals from different localities (Volkeskeld, Wehr, Niederzissen, Essinger Maare, Rieden II) from leucite phonolite tuffs of the Eifel volcanic complex, Germany, described in Bertelmann et al. (1985) and in Petrov and Hafner (1988). The orthoclase crystals were Fe-rich samples from Madagascar. Crystals of adularia (Orₓ=0.3, Abₓ=0.2, Caₓ=0.1) from Hybin pegmatite of the Kola peninsula were fragments from the larger crystal no. 1481/D, studied by Borutskyi et al. (1984). The albite samples from Amelia Court House, Virginia, U.S.A., were fragments of the same megacrystals as used by Petrov et al. (1989a, 1989b). Sanidine, hyalophane, orthoclase, adularia, and albite crystals were optically transparent, quite homogenous, and of gem quality.

The volumes of 87 single-crystal fragments cut for EPR experiments were about 1 mm³. The samples are (001) and (010) cleavage fragments spalled from larger crystals. Thin sections of the crystals were inspected optically for identification of the crystallographic axes; no inclusions or cracks were observed.

EXPERIMENTAL DETAILS

EPR spectra of single crystals were recorded on commercial X-band (between 4.2 and 295 K) and Q-band (at 295 K) spectrometers; details are described in Petrov and Hafner (1988). The applied magnetic field B for each recorded spectrum was calibrated by simultaneous measurement of B using a B-H15 field controller. The single crystals were aligned on a goniometer in the cavity of the spectrometer. They were rotated at different temperatures within the cryostat in the orthogonal laboratory system X₀, Y₀, Z₀. Their relation to the crystallographic axes has been reported earlier (Petrov et al., 1989b). Spectra were recorded every 10°; over critical ranges spectra were recorded every 1°-5°. The spin Hamiltonian parameters and direction cosines were obtained by matrix diagonalization.

Annihilation temperatures Tₐ of the paramagnetic centers were determined by stepwise annealing of the hydrocarbon-bearing microcline and hyalophane crystals in air. The annealing times at each temperature step were tₐ = 20 min. These conditions are the same as those of Maltash et al. (1981, 1982) and were chosen for a better correlation with their data. To create paramagnetic centers or to increase their concentration up to saturation, the crystals were exposed to X-ray or γ irradiation (60Co source) up to about 2 × 10⁶ Gray. To avoid surface effects for heat treatments and irradiation experiments, only single crystals were used.

RESULTS

In the investigated natural and irradiated single crystals of feldspar, thermally stable Fe³⁺ and Mn²⁺ centers and distinct metastable paramagnetic centers of the groups B, C, and D from Table 1, with different values of Tₐ and Tₓ, could be detected.

In natural hyalophane no EPR spectra of hydrocarbon radicals can be detected, neither in the temperature range between 4.2 and 295 K in the X band nor at 295 K in the Q band. In the region of g = 2, spectra of the NO₂ radical can be observed between 20 and 295 K, with Tₓ ≈ 70 K in the X band and at 295 K in the Q band. After X-ray and γ irradiation, the colorless crystals of heat-treated sanidine and thermally untreated hyalophane be-
Fig. 4. EPR spectra of natural microcline and hyalophane. The spectrum of microcline consists of a superposition of the spectra of CH₃, C₂H₅, (not resolved), and NO₂ radicals, rotation +e* || +Z₀, +a || +X₀, θ = 90°, m = 9.4965 GHz, T = 295 K. In natural hyalophane, only spectra of NO₂ radicals and h(bₐ) centers could be observed, rotation +a || +Z₀, +e* || +X₀, θ = 175°, m = 9.4071 GHz, T = 295 K. The color is produced by a' and d" centers; their spectra could be observed between 5 and 220 K, with Tₘ ≈ 60 K, like those in albite (Petrov et al., 1989b). In the irradiated hyalophane, spectra of methyl and ethyl radicals can be observed at 295 K. Centers of type h(bₐ) can be detected in the whole temperature range between 4.2 and 295 K, with Tₘ ≈ 5 K. In Figure 3 spectra of irradiated hyalophane, recorded at different values of Tₘ, are plotted. The broad signals or groups of signals in the region of g = 4 at d g ≈ 9 are caused by Fe³⁺ at T₁ and T₂ positions in monoclinic hyalophane, like those observed in sanidine (Petrov and Hafner, 1988).

In microcline from Hagendorf pegmatite a superposition of the spectra of the thermal metastable centers CH₃, C₂H₅, NO₂, a" h(cₐ), and e(m) are observable before or after artificial irradiation. In contrast to hyalophane, no Fe³⁺ signals can be found in any of the natural or irradiated hydrocarbon-bearing microcline crystals. Spectra of this type were reported first by Matyash et al. (1981, 1982) in microcline from granites and pegmatites from Ukrainian Shield, but the superposed spectra of CH₃ and C₂H₅ radicals were assigned to a NH₄⁺ cation radical at the M site and those of the NO₂ radical to N²⁻ at Dₐ O positions in the feldspar structure.

Organic radicals

CH₃ center. The four prominent lines in the spectrum of microcline shown in Figure 4 are approximately equally spaced, and they obviously form the quartet with the intensity ratio 1:3:3:1, as expected for the methyl radical (cf. Fig. 2). This quartet can be observed in the spectrum of natural microcline but in hyalophane only after X-ray or γ irradiation (Fig. 5, spectra b and c). The HF tensor A of the CH₃ center exhibits a small anisotropy; its average value is Aiso = -71 MHz for microcline and hyalophane. The individual peak to peak line widths, ΔBpp, are the same in both minerals. For different crystal orientations with respect to B, ΔBpp are anisotropic and vary between ΔBpp₁ = 1.5 - 2 × 10⁻⁴ T and ΔBpp₂ = 2 - 4 × 10⁻⁴ T for both the low-field (l) and the high-field (h) components, respectively. In polycrystalline spectra these values increase about 1.7 times: ΔBpp₁ = 2.5 - 4 × 10⁻⁴ T and ΔBpp₂ = 4 - 6 × 10⁻⁴ T. The ratios of line widths ΔBpp₁/ΔBpp₂ ≈ 1.5 and relative intensities I₁/I₄ ≈ 1.5 are the same in spectra of single crystals and of polycrystalline samples.

Eigenvalues of diagonalized g and T tensors of the CH₃ radical in microcline and hyalophane and their direction cosines are listed in Table 3. A comparison with the data of Matyash et al. (1981, 1982) is possible because they measured the central quartet, i.e., the 1:3:3:1 quartet of CH₃. However, they interpreted this quartet as one of the three quartets of NH₄⁺ with magnetic quantum number mₙ = 1, 0, -1 (see below).

Irradiation causes a significant increase of the relative intensity I₁ of the methyl spectrum in microcline. After irradiation with 1 × 10⁶ Gray, I₁ increased about 7.5 times, and saturation of the center concentration is at-
TABLE 3. Eigenvalues and direction cosines* of diagonalized $g$ and $T$ (MHz) tensors of CH$_3$ in microcline and hyalophane

<table>
<thead>
<tr>
<th>Feldspar</th>
<th>Eigenvalues</th>
<th>Direction cosines</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcline,</td>
<td>$g_x = 2.0089$</td>
<td>$0.95$ $0.04$ $-0.30$</td>
<td>this work</td>
</tr>
<tr>
<td>hyalophane</td>
<td>$g_y = 1.9992$</td>
<td>$0.05$ $0.99$ $0.00$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g_z = 2.0047$</td>
<td>$0.30$ $0.01$ $0.95$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_{xx} = 5.8$</td>
<td>$0.55$ $0.67$ $0.50$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_{yy} = -9.0$</td>
<td>$-0.82$ $0.36$ $0.44$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_{zz} = -3.1$</td>
<td>$0.11$ $-0.65$ $0.75$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_{xx} = -71$</td>
<td>$0.55$ $0.69$ $0.47$</td>
<td>Matyash et al.</td>
</tr>
<tr>
<td></td>
<td>$T_{xx} = 6.1$</td>
<td>$0.55$ $0.69$ $0.47$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_{yy} = -9.3$</td>
<td>$-0.83$ $0.40$ $0.38$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_{zz} = 3.3$</td>
<td>$0.07$ $-0.56$ $0.78$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_{xx} = -69$</td>
<td>$0.07$ $-0.56$ $0.78$</td>
<td></td>
</tr>
</tbody>
</table>

* $X \parallel a, Y \parallel b^*$ or $b$, respectively; $Z \parallel +a, ||(010)$.  ** $T_x$ values were calculated using the $A_{xx}$, $A_{yy}$, and $A_{zz}$ values from the original works.

Tained. Systematic heating experiments of single crystals show that this center is stable up to about 530 K. The signals disappear reversibly after heating to $T_a = 573$ K (Fig. 6); in the spectrum only the NO$_3$ triplet remains (cf. below). The same behavior is shown in the methyl spectrum of irradiated hyalophane.

**C$_2$H$_5$ center.** Q band spectra of irradiated hyalophane (Fig. 5, spectrum c) and untreated microcline single crystals (Fig. 7) are better resolved, and additional weak lines can be detected. A careful inspection of this subspectrum gives $A$ values and intensity ratios of the HF components that are typical for the ethyl radical. This spectrum is similar to the 12-line spectrum of ethyl radicals, with nonequivalent $\alpha$ and $\beta$ protons trapped in $\gamma$-irradiated silica gel and silica glass, giving an intensity ratio of 1:2:3:1:6:3:6:1:3:2:1 (cf. Eq. 6 and Fig. 2) and HF constants of $A_{\alpha\alpha} = -58.8$ MHz and $A_{\alpha\beta} = 73.4$ MHz (Joppen and Willard, 1972). For certain orientations, the spectrum with $N_{HFS} = 12$ is changed into a spectrum with $N_{HFS} = 6$. Its intensity ratio is close to the binomial ratio 1:5:10:10:5:1, indicating equal coupling of the unpaired electron with the five protons (Fig. 5, spectrum b). This effect appears in both minerals.

The ratio of relative line intensities $I_{rel}$ of methyl and ethyl spectra is found to be $I_{rel}^{CH_3}:I_{rel}^{C_2H_5} \approx 0.25$ in both minerals. Superposition of both spectra leads to a relatively complex HFS pattern (Figs. 5, spectrum c, and 7) with an intensity ratio of 1:6:3:1:18:3:3:18:1:3:6:1, schematically shown in Figure 2.

Fig. 6. EPR spectra of microcline heat treated at various annihilation temperatures $T_a$ at constant annihilation times $t_a = 20$ min. Rotation $+b^* \parallel +Z^*$, $+a \parallel +X^*$, $\theta = 167^\circ$, $m = 9.5239$ GHz, $T = 295$ K.

Fig. 7. EPR spectrum of natural microcline. The superposition of the CH$_3$ and C$_2$H$_5$ spectra is schematically marked (cf. Fig. 2). Experimental conditions as in Fig. 5, spectrum c.
Analogous to CH$_3$ centers, C$_2$H$_5$ centers in microcline and hyalophane have the same values of $A_{\text{iso}}$ and $\Delta B_{\text{iso}}$. For different crystal orientations with respect to B, $\Delta B_{\text{iso}}$ shows small anisotropy and varies between 4 and 6 × $10^{-4}$ T. In polycrystalline spectra the lines of $\alpha$ protons were averaged by anisotropic effects, and only the quartet with the intensity ratio of approximately 1:3:3:1 can be observed (Fig. 8). The behavior of C$_2$H$_5$ centers after heat treatment and irradiation is the same as that described for CH$_3$ centers.

Exact determination of g and T tensors of the ethyl radical and their direction cosines was not possible because of overlapping of the CH$_3$, C$_2$H$_5$, and NO$_2$ room-temperature spectra in both minerals. Low-temperature measurements between 5 and 250 K led to additional overlapping with the 11-line spectra of a$^+$ and d$^-$ type O$^{1-}$/2$^{27}$Al centers, complicating the interpretation further.

The 12-line spectrum observed in microcline, interpreted as NH$_4^+$ by Matyash et al. (1981, 1982), shows the same behavior after heat treatment and irradiation as the spectra of hydrocarbons in this paper.

**Inorganic radicals**

O$^{1-}$/2$^{27}$Al center. The typical 11-line HFS spectrum of distinct O$^{1-}$/2$^{27}$Al centers is present in nearly all irradiated ordered and disordered feldspars. This spectrum can be observed mainly between 5 and 220 K. The temperature of maximum intensity was $T_m = 60$ K in all feldspars studied (cf. Table 1). However, in Fe-rich orthoclase from Madagascar and adularia from Hybin pegmatite with Fe$_2$O$_3$ contents of 1–3 wt% (FeO up to 0.25 wt%), no O$^{1-}$/2$^{27}$Al centers (or only a very small concentration) and no smoky color was formed after irradiation.

Natural and irradiated alkali feldspars show two main types of O$^{1-}$/2$^{27}$Al EPR spectra: (1) spectra of a$^+$, c$^+$, c$^-$, d$^-$, and d$^+$ centers with an intensity ratio 2:2:2:1:1, and (2) spectra of a$^+$ and d$^-$ centers with an intensity ratio of 3:1. Until now spectra of type 1 have been detected only in well-ordered albite. Spectra of type 2 are observable in ordered and disordered feldspar with large M cations.

In low Amelia albite, spectra of type 1 consist of four sets of superposed 11 HFS patterns because of the distinct O$^{1-}$/2$^{27}$Al centers (Fig. 9), discussed in detail by Petrov et al. (1989b). In all feldspars with large M cations ($M = K, Ba$), independent of the degree of Al-Si order, only spectra of 14–15 lines can be observed in certain directions (Fig. 10), created by superposition of the 11-line HFS spectra of two O$^{1-}$/2$^{27}$Al centers at distinct O positions. The eigenvalues and eigenvectors of the diagonalized g tensor of the centers in microcline, sanidine, and hyalophane are listed in Table 4. Comparison of the direction cosines of the eigenvectors $g_{\text{eig}}$ of the g tensor and T-T directions in the feldspar structure yields an assignment of the centers to O at the Al and D0 position, i.e., a$^+$ and d$^-$ centers (cf. Fig. 1). Their spectra exhibit an intensity ratio a$^+$/d$^-$ of about 3:1. The a$^+$ centers with the same or similar Hamiltonian parameters were detected in various feldspars by Speit and Lehmann (1982) but were described as b$^+$. Their criteria for assigning the cen-
PETROV: LATTICE-STABILIZED RADICALS IN FELDSPAR

Table 4. Eigenvalues and direction cosines* of the diagonalized g tensor of a" and d\(d\) centers at 60 K

<table>
<thead>
<tr>
<th>Feldspar</th>
<th>PC</th>
<th>Eigenvalues</th>
<th>Direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcline</td>
<td>a(a)</td>
<td>(g_{xx} = 2.0004)</td>
<td>X: 0.74, Y: 0.20, Z: 0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(g_{yy} = 2.0056)</td>
<td>X: -0.05, Y: 0.86, Z: 0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(g_{zz} = 2.0259)</td>
<td>X: 0.49, Y: 0.47, Z: 0.73</td>
</tr>
<tr>
<td>Sanidine</td>
<td>a(d)</td>
<td>(g_{xx} = 1.9937)</td>
<td>X: 0.77, Y: 0.38, Z: 0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(g_{yy} = 2.0081)</td>
<td>X: 0.45, Y: 0.86, Z: 0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(g_{zz} = 2.0259)</td>
<td>X: 0.49, Y: 0.47, Z: 0.73</td>
</tr>
<tr>
<td>Hyalophane</td>
<td>a(d)</td>
<td>(g_{xx} = 1.9994)</td>
<td>X: 0.70, Y: 0.79, Z: 0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(g_{yy} = 2.0063)</td>
<td>X: 0.31, Y: 0.47, Z: 0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(g_{zz} = 2.0257)</td>
<td>X: 0.67, Y: 0.71, Z: 0.19</td>
</tr>
</tbody>
</table>

Note: PC = paramagnetic center.
* See Table 3.

Fig. 10. Typical EPR spectrum of the O\(/-/^{27}\)Al centers a\(a\) and d\(d\) in \(\gamma\) irradiated ordered and disordered feldspars with large M cations (M = K, Ba), e.g., microcline, sanidine, and hyalophane. Rotation \(+e^* || +Z', +a || +X'; \theta = 45^\circ; m = 9.2457\ GHz, T = 60 K.

Fig. 11. Stereographic projection of the g eigenvectors from Table 4 of (a) a\(a\) centers in sanidine (triangles), microcline (circles), and hyalophane (squares) and (b) of d\(d\) centers in sanidine (triangles) and hyalophane (squares).
TABLE 5. Eigenvalues and direction cosines* of the diagonalized g tensor of O−/(Si,M2+) centers in various feldspars

<table>
<thead>
<tr>
<th>Feldspar</th>
<th>PC</th>
<th>Eigenvalues</th>
<th>Direction cosines</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labradorite,</td>
<td>h(bo)</td>
<td>gxx = 1.9917</td>
<td>X: -0.35</td>
<td>Speit and Lehmann</td>
</tr>
<tr>
<td>oligoclase</td>
<td></td>
<td>gyy = 2.0101</td>
<td>Y: -0.48</td>
<td>(1982)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>gzz = 2.0193</td>
<td>Z: 0.80</td>
<td>this work</td>
</tr>
<tr>
<td>Amazonite</td>
<td>h(bn)</td>
<td>gxx = 2.0040</td>
<td>-0.17</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>gyy = 2.0103</td>
<td>0.92</td>
<td>Matyash et al.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>gzz = 2.0123</td>
<td>0.92</td>
<td>(1981, 1982); this</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>work</td>
</tr>
<tr>
<td>Hyalophane</td>
<td>h(b)</td>
<td>gxx = 2.0032</td>
<td>0.30</td>
<td>Petrov et al.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>gyy = 2.0140</td>
<td>0.99</td>
<td>(1989b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>gzz = 2.0077</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Microcline</td>
<td>h(cno)</td>
<td>gxx = 2.0077</td>
<td>-0.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>gyy = 2.0228</td>
<td>-0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>gzz = 2.0618</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Albite</td>
<td>h(cn)</td>
<td>gxx = 2.0077</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>gyy = 2.0228</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>gzz = 2.0618</td>
<td>0.34</td>
<td></td>
</tr>
</tbody>
</table>

Note: PC = paramagnetic center.
* See Table 3.

cate. The widths of the individual lines are \( \Delta B_{pp} = 4 \pm 0.5 \times 10^{-4} \) T; \( \Delta B_{pp} \), as well as \( A_{iso} \), did not change between 5 and 220 K. This indicates that the lifetime of the excited states does not influence \( \Delta B_{pp} \). The large line widths observed in all feldspars compared with those of Al centers in, e.g., smoky quartz (e.g., Mackey, 1963; Schnadt and Schneider, 1970) must be due to other phenomena, most probably to unresolved HF interactions with nuclear magnetic moments of adjacent atoms (e.g., Na,Al) or to some disorder in the Al-Si occupancy of adjacent tetrahedra.

\( \text{O}^{−}/(\text{Si},\text{M}^{2+}) \) center. In addition to the \( \text{O}^{−}/27\text{Al} \) centers distinct \( \text{O}^{−}/(\text{Si},\text{M}^{2+}) \) centers were found in all investigated crystals of ordered and disordered feldspars. The spectrum of these centers consists of one single line (\( \Delta B_{pp} = 6 \pm 0.5 \times 10^{-4} \) T) and can be observed between 5 and 295 K with \( T_m \approx 5 \) or 115 K for different feldspars. No HFS could be detected in this temperature range. The angular dependence of the spectrum on crystal rotation with respect to \( B \) is described by the first term, \( \mathbf{BBgS} \), of Equation 2.

Centers of this type were described as existing in irradiated microcline, labradorite, oligoclase, and albite (Marfunin and Bershov, 1970; Speit and Lehmann, 1982; Petrov et al., 1989b). Eigenvalues and direction cosines of the diagonalized g tensor of this center in different feldspars with respect to T-O directions in the feldspar structure are presented in Table 5. The data from the center in microcline from the Hagendorf pegmatite are approximately the same as those of microcline from granites and pegmatites of the Ukrainian Shield (Matyash et al., 1981, 1982). The stereographic projections of the eigenvalues of the g tensor of this center for various feldspars are plotted in Figure 12.

\( \text{NO}_2 \) center. As shown in Figure 6, in the spectrum of microcline the methyl and ethyl signals disappear after heating at \( T_\lambda = 573 \) K. In heat-treated microcline and untreated hyalophane (Figs. 4 and 5, spectrum a), the typical spectrum of \( \text{NO}_2 \) could be observed. The \( \text{NO}_2 \) center can be identified by its characteristic HFS spectrum of three equidistant lines of equal intensity. A HFS pattern of this type is due to the interaction of an unpaired electron (\( S = \frac{1}{2} \)) with a N nucleus (I = 1, 99.63% natural abundance of \(^{14}\text{N}\)). Analogous to hydrocarbon centers, \( \text{NO}_2 \) centers in microcline and hyalophane have the same values of \( A_{iso} \) and \( \Delta B_{pp} \). For different crystal orientations with respect to \( B \), \( \Delta B_{pp} \) is anisotropic and varies between 5 and \( 10 \times 10^{-4} \) T.

A spectrum of this type was observed first in microcline.
from Ukrainian Shield granites and pegmatites by Matyash et al. (1981, 1982) and interpreted as \(\text{N}^2^-\). Comparison of the EPR data of Matyash et al. (1981, 1982) and Hamiltonian parameters of N-associated paramagnetic centers in different host crystals (Table 6) shows evidently that their center is also NO\(_2\). The direction cosines of the diagonalized \(g\) and T tensors of the NO\(_2\) radical in hyalophane and microcline from Hagendorf pegmatite (Table 7) are in good agreement with the data of Matyash et al. (1981, 1982).

The calculated values of \(c^2\), \(c^4\), and \(\rho\) from Equations 4, 5, 7, and 8 for NO\(_2\) in hyalophane and microcline at various temperatures are given in Table 8. These values are typical for triatomic radicals with 17 valence electrons (Atkins and Symons, 1967; Carrington and McLachlan, 1967) and may be compared with the data for NO\(_2\) in beryl (Suharzhevsky, 1976; Solntsev, 1981). The O-N-O angles \(\rho\) estimated on the basis of Equation 8 for various temperatures are between 129–138 and 130–140° for hyalophane and microcline, respectively (Table 8).

**Table 6.** Hamiltonian parameters of N-associated paramagnetic centers in various matrices

<table>
<thead>
<tr>
<th>Host crystal</th>
<th>PC</th>
<th>(T) (K)</th>
<th>(g_{xx})</th>
<th>(g_{yy})</th>
<th>(g_{zz})</th>
<th>(T_{xx})</th>
<th>(T_{yy})</th>
<th>(T_{zz})</th>
<th>(A_{\text{iso}})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>N</td>
<td>2.0035</td>
<td>2.0025</td>
<td>2.0014</td>
<td>-1.7</td>
<td>-1.7</td>
<td>3.4</td>
<td>18.5</td>
<td>Poole et al. (1977)</td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td>N</td>
<td>2.0020</td>
<td>2.0020</td>
<td>2.0020</td>
<td>-10.2</td>
<td>-10.2</td>
<td>20.4</td>
<td>86.1</td>
<td>Poole et al. (1977)</td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td>C-N-N-C</td>
<td>2.0030</td>
<td>2.0030</td>
<td>2.0030</td>
<td>-12.6</td>
<td>-12.6</td>
<td>25.2</td>
<td>96.3</td>
<td>Poole et al. (1977)</td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td>N-C-N</td>
<td>2.0028</td>
<td>2.0028</td>
<td>2.0028</td>
<td>-11.3</td>
<td>-11.3</td>
<td>22.6</td>
<td>93.0</td>
<td>Poole et al. (1977)</td>
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</tr>
<tr>
<td>KN(_2)</td>
<td>(\text{N}^2^-)</td>
<td>2.0027</td>
<td>2.0008</td>
<td>1.9832</td>
<td>-14.6</td>
<td>-15.01</td>
<td>29.7</td>
<td>3.92</td>
<td>Atkins and Symons (1967)</td>
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</tr>
<tr>
<td>Beryl</td>
<td>NO(_2)</td>
<td>77</td>
<td>2.0213</td>
<td>2.0213</td>
<td>2.0223</td>
<td>-1.0</td>
<td>-1.0</td>
<td>1.9</td>
<td>11.3</td>
<td>Solntsev (1981)</td>
</tr>
<tr>
<td>Pb(NO(_3))</td>
<td>NO(_2)</td>
<td>77</td>
<td>2.0299</td>
<td>2.0297</td>
<td>1.998</td>
<td>-2.0</td>
<td>-2.0</td>
<td>3.6</td>
<td>4.8</td>
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</tr>
<tr>
<td>KNO(_2)</td>
<td>NO(_2)</td>
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<td>2.0087</td>
<td>2.0107</td>
<td>2.007</td>
<td>-26.6</td>
<td>-26.6</td>
<td>53.2</td>
<td>36.4</td>
<td>Ayscough (1967)</td>
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<tr>
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<td>83</td>
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<td>2.0068</td>
<td>2.0020</td>
<td>-19.6</td>
<td>-19.6</td>
<td>37.2</td>
<td>159.3</td>
<td>Ayscough (1967)</td>
</tr>
<tr>
<td>Ice</td>
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<td>1.9920</td>
<td>2.0022</td>
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<td>-17.6</td>
<td>32.0</td>
<td>151.7</td>
<td>Ayscough (1967)</td>
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<tr>
<td>NaNO(_3)</td>
<td>NO(_2)</td>
<td>77</td>
<td>2.0057</td>
<td>1.9910</td>
<td>2.0015</td>
<td>-14.8</td>
<td>-22.1</td>
<td>36.9</td>
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<tr>
<td>KNO(_3)</td>
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<td>77</td>
<td>2.0036</td>
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<td>2.0036</td>
<td>-11.1</td>
<td>-11.1</td>
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<td>153.1</td>
<td>Wertz and Bolton (1972)</td>
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<tr>
<td>AgNO(_3)</td>
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<td>2.0090</td>
<td>1.9978</td>
<td>2.0093</td>
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<td>-21.8</td>
<td>37.2</td>
<td>157.6</td>
<td>Pietrzak and Wood (1970)</td>
</tr>
<tr>
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<td>NO(_2)</td>
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<td>2.0043</td>
<td>1.9922</td>
<td>2.0051</td>
<td>-13.4</td>
<td>-18.8</td>
<td>32.5</td>
<td>156.5</td>
<td>Pietrzak and Wood (1970)</td>
</tr>
<tr>
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<td>2.0017</td>
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<td>156.2</td>
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</tr>
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<td>1.9925</td>
<td>2.0020</td>
<td>-12.6</td>
<td>-18.8</td>
<td>31.4</td>
<td>152.6</td>
<td>Suharzhevsky (1976), Solntsev (1981)</td>
</tr>
<tr>
<td>Microcline†</td>
<td>NO(_2)</td>
<td>77</td>
<td>2.0067</td>
<td>1.9922</td>
<td>2.0006</td>
<td>-6.7</td>
<td>-21.8</td>
<td>28.6</td>
<td>164.6</td>
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</tr>
<tr>
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<tr>
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<td>30</td>
<td>2.0048</td>
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<td>2.0011</td>
<td>-7.7</td>
<td>-21.9</td>
<td>29.8</td>
<td>170.7</td>
<td>this work</td>
</tr>
</tbody>
</table>

Note: PC = paramagnetic center.

* See Table 3.

** Cited as \(\text{N}^2^-\) in Matyash et al. (1981).

† Interpreted as \(\text{N}^2^-\).

---

**Table 7.** Eigenvalues and direction cosines of the diagonalized \(g\) and T (MHz) tensors of NO\(_2\) with \(\rho = 138^\circ\) in microcline and hyalophane at different temperatures

<table>
<thead>
<tr>
<th>Feldspar</th>
<th>(T) (K)</th>
<th>Eigenvalues</th>
<th>(X)</th>
<th>(Y)</th>
<th>(Z)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcline*</td>
<td>77</td>
<td>(g_{xx} = 2.006)</td>
<td>0.27</td>
<td>0.96</td>
<td>0.02</td>
<td>Matyash et al. (1981, 1982)</td>
</tr>
<tr>
<td>Microcline</td>
<td>77</td>
<td>(g_{xx} = 2.006)</td>
<td>0.96</td>
<td>0.27</td>
<td>-0.02</td>
<td>this work</td>
</tr>
<tr>
<td>Hyalophane</td>
<td>30</td>
<td>(g_{xx} = 2.0048)</td>
<td>0.38</td>
<td>0.92</td>
<td>0.00</td>
<td>this work</td>
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</tbody>
</table>

* See Table 3.
Table 8. Calculated unpaired electron-spin density coefficients $c_3^2$, $c_5^2$, and $c_6^2$ and O-N-O bond angles $\rho$ of the NO$_2$ radical in hyalophane, microcline, and beryl at various temperatures.

<table>
<thead>
<tr>
<th>Host crystal</th>
<th>$T$ (K)</th>
<th>$c_3^2$</th>
<th>$c_5^2$</th>
<th>$c_6^2$</th>
<th>$\lambda$</th>
<th>$\rho$ (°)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyalophane</td>
<td>295</td>
<td>0.094</td>
<td>0.322</td>
<td>0.584</td>
<td>3.430</td>
<td>129</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.095</td>
<td>0.349</td>
<td>0.556</td>
<td>3.678</td>
<td>130</td>
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<tr>
<td></td>
<td>77</td>
<td>0.096</td>
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<td>0.095</td>
<td>0.472</td>
<td>0.433</td>
<td>4.967</td>
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<td></td>
<td>30</td>
<td>0.094</td>
<td>0.537</td>
<td>0.369</td>
<td>5.710</td>
<td>137</td>
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<tr>
<td>Microcline</td>
<td>295</td>
<td>0.092</td>
<td>0.328</td>
<td>0.580</td>
<td>3.565</td>
<td>130</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.093</td>
<td>0.334</td>
<td>0.573</td>
<td>3.572</td>
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<tr>
<td></td>
<td>77</td>
<td>0.092</td>
<td>0.532</td>
<td>0.376</td>
<td>5.770</td>
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<tr>
<td></td>
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<td>0.093</td>
<td>0.598</td>
<td>0.309</td>
<td>6.430</td>
<td>140</td>
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<tr>
<td></td>
<td>30</td>
<td>0.093</td>
<td>0.610</td>
<td>0.297</td>
<td>6.559</td>
<td>138</td>
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<tr>
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<td>0.090</td>
<td>0.320</td>
<td>0.590</td>
<td>3.562</td>
<td>130</td>
<td>Matyash et al. (1981, 1982)</td>
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<td>0.091</td>
<td>0.515</td>
<td>0.394</td>
<td>5.661</td>
<td>138</td>
<td>Suharzhevskyi (1976), Solntsev (1981)</td>
</tr>
<tr>
<td>Beryl*</td>
<td>77</td>
<td>0.084</td>
<td>0.565</td>
<td>0.351</td>
<td>6.726</td>
<td>140</td>
<td></td>
</tr>
</tbody>
</table>

* The $c_3^2$, $c_5^2$, $c_6^2$, and $\rho$ values from Eqs. 4, 5, 7, and 8 were calculated using the original data and the corrected $^{14}A_{1u}$ and $^{14}T$ for the free N atom after Morton and Preston (1978).

The NO$_2$ center is observable in natural single crystals and polycrystalline samples. Irradiation with a $\gamma$ dose up to about $2 \times 10^6$ Gray causes the spectrum intensity to decrease by a factor of 16 (cf. spectra a and b in Fig. 5). The annihilation temperature of the center is $T_a \approx 873$ K. After being heated above this temperature, the center is destroyed irreversibly. Heat treatment at about 823 K causes an increasing of the signal intensity of about 50% (Fig. 13). The same behavior showed the center described by Matyash et al. (1981).

SiO$_3^-$ center. An electron captured at an O vacancy of the SiO$_4$ tetrahedron forms the 25-electron radical SiO$_3^-$. A center of this type with additional HFS from one adjacent $^{27}$Al nuclei was detected in microcline by Matyash et al. (1981, 1982). The center was attributed to an electron captured at a vacancy on the BO O position, forming an e(b$_0$) center. The same center, but without HFS from a neighboring $^{27}$Al nucleus, can also be detected in the spectra of most feldspars studied, but, because of the absence of HFI with $^{27}$Al, this center must be attributed to an O vacancy at an O$_0$ position (e$_m$ center) in the feldspar structure. The approximately isotropic $g$ allows no unambiguous assignment of this center to specific O vacancies.

Discussion

Hydrocarbon radicals

The typical 12-line spectrum of ethyl radicals with the intensity ratio of 1:2:3:1:6:3:3:6:1:3:2:1 was observed in microcline first by Matyash et al. (1981, 1982), though it was assigned to NH$_3^+$ radicals at M positions (Fig. 14b). However, it is generally assumed that, because of the rotation of the NH$_3^+$ radical, the three protons are equivalent. In this case, the HF interaction between S and I leads to multiple sets of $(2I_n + 1)(2nI_{1h} + 1)$ lines. Because $I_n = 1$, $I_{1h} = \frac{1}{2}$, and $n = 3$, the NH$_3^+$ spectrum consists of three quartets (1:3:3:1) of equal intensities, corresponding to the three allowed orientations of the $^{14}$N nuclear spin (magnetic quantum number $m_n = -1, 0, 1$) with respect to B. The typical NH$_3^+$ spectrum with an intensity ratio of 1:1:3:1:3:3:3:1:1:1 is caused by the disposition of the three quartets. Such a spectrum, caused by NH$_3^+$ trapped in a single crystal of NH$_4$ClO$_4$, is shown in Figure 14a. The same spectrum was reported for NH$_3^+$ in structural channels of beryl (Solntsev, 1981). However, these centers are thermally much more stable than those reported by Matyash et al. (1981, 1982); their annihilation temperature is 1.6 times higher. After heat treatment at 773 K, NH$_3^+$ decays into NH$_2$ + H$^+$, and the characteristic spectrum of NH$_2$ can be observed. This
feature cannot be seen in spectra of microcline. The behavior after heat treatment and irradiation of the centers described by Matyash et al. (1981, 1982) is exactly the same as those of the hydrocarbon centers reported in this paper.

A careful inspection of the spectrum of Matyash et al. (1981 and 1982, their Figs. 46 and 1, respectively) shows an intensity ratio of the lines that is typical for the ethyl radical (cf. Figs. 2 and 14b). The ratio $A_{2g}/A_{2u} = 0.8$ of $\alpha$ and $\beta$ protons of the ethyl radical is in good agreement with the results of this paper and with theoretical and experimental data (Jen et al., 1958; Fessenden and Schuler, 1963; Bersohn and Baird, 1966; Ayscough, 1967; Carrington and McLachlan, 1967; Wertz and Bolton, 1972).

For free radicals in fluids of low viscosity, the molecular tumbling rate is sufficiently rapid that the anisotropic $g$ and $T$ are averaged to zero. Line widths of $\Delta B_{pp} \approx 0.1 \times 10^{-4}$ T or less are common (e.g., Ayscough, 1967). In fluids of moderate viscosity, the tumbling rate decreases, and $\Delta B_{pp}$ increases ($\approx 0.3 \times 10^{-4}$ T) (e.g., Fessenden and Schuler, 1963). For radicals trapped in single crystals the
tumbling rate decreases further, and deviation of $\Delta g_0$ and $T_1$ from zero is evident, accordingly the value of $\Delta B_{pp}$ increases. However, $\Delta B_{pp}$ is proportional to the mean square of the shift in line positions and is different for each line. If $A_{iso}$ is positive, the high-field HF components are broader, i.e., the derivate amplitude is lower (Wertz and Bolton, 1972). In spectra of randomly oriented polycrystalline matrices these effects are more pronounced.

In the hydrocarbon spectra of single crystals of microcline and hyalophane the influence of these effects is evident. In comparison with the values expected for hydrocarbon radicals in fluids, $\Delta B_{pp}$ of low- and high-field components of the central quartet are up to 20 and up to 40 times broader, respectively. Asymmetry in line shape and width and therefore in the line intensities of the quartet is caused by the superposition of the spectra of $\alpha$ protons of the methyl radical and $\beta$ protons of the ethyl radical. Because the rotation of $\beta$ protons is fixed in a plane perpendicular to the C-C axis, their rotation in the larger ethyl radical, trapped in a single crystal, is more constrained than the relatively freely rotating $\alpha$ protons of the methyl radical. Therefore the HFI of the $\alpha$ protons of the methyl radical has a smaller anisotropy, each quartet is nearly symmetric, and the values of $\Delta B_{pp}$ are smaller. On the other hand, the anisotropy of HFI of the $\beta$ protons of the ethyl radical is larger, and the values of $\Delta B_{pp}$ increase and are different for each component. This causes the asymmetry in line shape and intensity of the central quartet in the superposed spectra of methyl and ethyl radicals. Because of the positive sign of $A_{iso}$, the high-field components have larger $\Delta B_{pp}$ and lower $I_{iso}$ values than those of the low-field components of the quartet.

By overlapping of methyl and ethyl spectra in microcline and hyalophane, the anisotropic effects dominate and explain the asymmetry of the spectra. In polycrystalline spectra these effects are evident. The approximately equal $A_{iso}$ and $T_1$, values of the $\alpha$ protons in the $-CH_2$ group lead to additional line broadening (up to 60 times broader than in fluids) in the single-crystal spectra of both minerals. Consequently, in their polycrystalline spectra the random orientation of $T$ with respect to $B$ causes an extreme line broadening; no lines of the ethylene group could be detected. Only the superposition of the spectra of the $\alpha$ and $\beta$ protons of the methyl and ethyl radicals, respectively, could be observed (Fig. 8).

The organic free radicals, by virtue of their great reactivity, are not stable in fluids (inclusions) and are not stabilized by surfaces of solid substrates at room temperature. In almost all cases, spectra of these radicals can be detected only after continued ionizing irradiation at low temperatures (<200 K). The average lifetime of methyl and ethyl radicals in fluids at temperatures <200 K is about $10^{-3}$ s (Fessenden and Schuler, 1963; Bljumenfeld et al., 1966; Ayscough, 1967; Wertz and Bolton, 1972). The lifetime of methyl and ethyl radicals adsorbed in silica gel during $\gamma$ irradiation at 77 K is a few minutes after reaching <260 K (Bljumenfeld et al., 1966; Joppien and Willard, 1972). After warming from 77 to 129 K,
T2m. Centers of this type may be formed where two adjacent tetrahedral positions on either side of an O atom are occupied by Al atoms, building an Al-O-Al bridge. The detectable HF interaction of the electronic spins of O\(^{1/2}\) centers with nuclear magnetic moments of two neighboring \(^{27}\)Al and their assignments to crystallographic positions based on comparison of the direction cosines of the \(g\) tensor and T-T directions (Fig. 1) allow the direct measurement of the Al migration, e.g., the exchange of Al and Si among the tetrahedral sites in order-disorder processes.

The values of line width \(\Delta B_{pp}\), HF coupling constant \(A\), and center concentration and therefore \(T_m\) of the O\(^{1/2}\)/\(^{27}\)Al centers are approximately equal in all feldspars studied, independent of their degree of long-range Al-Si order. This indicates a similar degree of Al-Si order around the center; i.e., in all feldspars such centers can be formed only in intracrystalline domains of similar order. If such domains can be considered as frozen states of Al distribution then the position and frequency of different Al-O'\(^{-}\)Al fragments may yield information about short-range Al site occupancy and, therefore, about ordering paths in feldspar. The intensity ratio of the HFS spectra of \(a_t^1, a_t^2, c_o, d_m, c_m,\) and \(d_m\) centers, i.e., the ratio of their concentrations, allows the direct measurement of Al site occupancies at definite tetrahedral positions. The short-range Al site occupancy in potassium feldspar and barium feldspar in a short EPR length scale (for Al-O'\(^{-}\)-Al bridges on the order of 10\(^{-6}\) pfu) is approximately equal to \(t_o \approx t_m \approx t_o \approx t_m\). Here, \(t_o, t_m, \) etc., refer to the site occupancies of Al at positions T10, T1m, etc., respectively. This suggests a short-range ordering path of the intermediate two-step trend (e.g., Ribbe, 1983; Kroll and Ribbe, 1983). In low albite with \(t_o \approx t_m > t_o \approx t_m\) the ordering path tends more to the one-step trend. However, to answer this question with certainty, a comparison with other methods is necessary.

The absence (or very low concentration) of O\(^{1/2}\)/\(^{27}\)Al centers in Fe-rich orthoclase and adularia after long-term irradiation may be explained by a possible constant of the positive charge deficiency in the Al-O-Al segments that violate the principle of Loewenstein by the substitution of Fe\(^{2+}\) for K\(^{1+}\), i.e., K\(^{1+}\) + Si\(^{4+}\) \(\rightarrow\) Fe\(^{2+}\) + Al\(^{3+}\), similar to the case of amazonite with high Pb\(^{2+}\) content (Petrov et al., 1993). Thus, no stable O\(^{1/2}\)/\(^{27}\)Al centers and, therefore, no smoky color can be induced by irradiation. In orthoclase and adularia with sluggish Al-Si exchange kinetics and high Fe\(_2\)O\(_3\) content, the line intensity of Fe\(^{2+}\) at the T1 tetrahedral position is about ten times higher than those of Eifel sanidine with anomalous rapid Al-Si exchange kinetics (Petrov, in preparation). The Fe\(_2\)O\(_3\) tetrahedron (Fe-O = 1.862 Å) has a quasi-orthorhombic distortion of 9.3° from cubic symmetry of the two opposite tetrahedral angles O-Fe-O (Petrov and Hafner, 1988). At the boundaries between ordered and disordered domains in the feldspar structure, such an angular distortion of the tetrahedron can have a stabilizing effect. A similar effect was found for Fe\(^{3+}\)O\(_2\) tetrahedra with quasi-orthorhombic distortion embedded in the boundaries between ordered and disordered sections of the SiO\(_2\) matrix in acid volcanic glasses (Bershov et al., 1983).

The Al-Si exchange in feldspar seems to be facilitated by O\(^{1/2}\)/\(^{27}\)Al centers, OH\(^-\), and H\(_2\)O (Beran, 1986; Petrov and Hafner, 1988), whereas Fe\(^{3+}\) obviously can have a stabilizing effect. Furthermore, with increasing total Fe\(_2\)O\(_3\) content the concentration of O\(^{1/2}\)/\(^{27}\)Al centers decreases and the Al-Si exchange kinetics becomes more sluggish.

In all investigated natural and irradiated feldspars with different degrees of Al-Si order distinct O\(^{1/2}\)-(Si,M\(^{2+}\)) centers are present. Since the center is apparently not perturbed by HFI with an adjacent nuclear moment, it is generally assumed that it occurs at O positions that are not bridging to Al tetrahedra. For O\(^{1/2}\) stabilization at room temperature a charge of <3+ at one of the adjacent tetrahedral positions is needed. Divalent ions that possess abundant isotopes without nuclear moments are most likely for M, e.g., Mg\(^{2+}\) or a divalent cation with a small radius at a T1m position. The O\(^{1/2}\)-(Si,M\(^{2+}\)) center without HFS of the adjacent \(^{27}\)Al most probably can be created at D\(_m\), C\(_m\), B\(_m\), or A\(_m\) O positions. In the investigated crystals of feldspar, the \(g \_m\) eigenvalues of the \(g\) tensor of the 31-electron radical SiO\(_2\)\(^{-}\) can be attributed to the T20-Bm, T20-Cm, and T20-Dm directions. The O\(^{1/2}\)-(Si,M\(^{2+}\)) centers in most feldspars investigated so far with different degrees of Al-Si order are \(h(b_m), h(c_m),\) and \(h(d_m)\) centers (Table 5). The \(h(b_m)\) centers in labradorite and oligoclase were determined as \(h(b_m)\) by Speit and Lehmann (1982). In this case, however, HFS due to interaction with at least one adjacent \(^{27}\)Al nuclei at the T10 position should be observable in the spectra (cf. Fig. 1).

NO\(_2\) radicals

Matyash et al. (1981, 1982) attributed the triplet in the spectrum of heat-treated microcline (Fig. 6) to a N\(^{2-}\) center at the Dm O position (Si-N\(^{2-}\) -Si). Matyash et al. (1981, their Table 13) based their interpretation on a comparison with Hamiltonian parameters of N\(^{2-}\) centers from Atkins and Symons (1967). However, in the original work N\(^{2-}\) centers are not reported; the parameters cited are from N\(^{2-}\) pairs. This comparison is retracted by Matyash et al. (1982).

For NO\(_2\) in different host crystals HF constants were measured (Table 6) that correspond to coefficients of \(c_2\) between 0.084 and 0.1. The large s-fraction \(c_2\) in the wave function of the unpaired N electron and the relatively small 2p/2s ratio \(\lambda\) (Table 8) is characteristic only for the NO\(_2\) radical (Atkins and Symons, 1967; Aycough, 1967; Wertz and Bolton, 1972). The molecular parameters and O-N-O angles of NO\(_2\) in microcline and hyalophane (Table 8) are in good agreement with published data of NO\(_2\) in many host matrices (e.g., Atkins and Symons, 1967). Contrary to these data, the unpaired elec-
tron of other NO₃ radicals listed in Table 6 is localized in an orbital with a predominant p fraction. For example, values of \( c_t^2 = 0.026 \), \( c_{pe}^2 = 0.54 \), and \( \lambda_t^2 = 24 \) were calculated for NO₃⁻ centers in single crystals of NaCl and KNO₃; i.e., the unpaired electron is located in a nearly pure p orbital. The remaining 40% of the electron density is delocalized at the O atoms (Atkins and Symons, 1967).

For the \(^{14}\)N⁠-⁠\(^\text{13}\)C bonding in type I diamond, Shcherbakova et al. (1969, 1972) determined values of \( A_\text{iso} \), corresponding to \( c_t^2 = 0.051 \). They localized the unpaired electron in an antibonded p orbital. Smith et al. (1959) investigated the same type of diamond and calculated 12.5% s and 87.5% p fraction for the \(^{14}\)NO⁻ hybrid.

The behavior of the spectrum after heat treatment and irradiation may be explained by the postulation of a substitution of NO₃ for K⁺. A part of these radicals can trap electrons by natural irradiation and is transformed into the diamagnetic NO₂⁻ state. These radicals can be regarded as electron centers, complementary to the distinct O⁻-hole centers (\( a_t^2, d_t^2, \) and \( h_t^2 \)) in the structure of microcline and hyalophane. Thus, compensation for the energetically unfavorable accumulation of positive charges at the O⁻ ion is given, and at low temperatures the hole is stabilized at this O atom. In addition, yielding of electrons transforms this part of the radicals into their paramagnetic form NO₂⁺:

\[
\text{NO}_2 + \text{NO}_2^- + O^- \rightarrow 2\text{NO}_2 + O^{2-}.
\] (9)

In accordance with this interpretation, heat treatments at \( T_A = 823 \text{ K} \) of irradiated crystals caused a decay in the spectra of all types of radiation-induced O⁻ centers and an increase in the line intensity of the NO₂ spectrum (Fig. 13). According to Equation 9, the remaining 50% of these radicals were transformed by heat treatment at 823 K into their paramagnetic state by recombination of NO₂⁻ electrons and O⁻-holes. Irradiation caused a significant decrease in the NO₂ spectrum (cf. Fig. 5, spectra a and b) and the creation of the distinct O⁻-centers with spectra of high intensity. The same behavior was reported by Matyash et al. (1981) for N²⁻ centers, but omitted in Matyash et al. (1982). After heat treatment at 873 K, all NO₂⁻ centers were destroyed irreversibly. After irradiation up to \( 2 \times 10^6 \text{ Gray} \), the centers cannot be restored. A possible model for the mechanism of center destruction may be given by

\[
\text{NO}_2 \rightarrow \text{NO} + \frac{1}{2}\text{O}_2.
\] (10)

In fluids NO₃ tends to form dimers rapidly, producing diamagnetic NO₂⁻. Isolated NO₃ free radicals can be produced in situ only by ionizing irradiation at low temperatures (4.2-77 K) in crystals of nitrates or other compounds doped with traces of NO₃ (Atkins and Symons, 1967; Ayscough, 1967; Wertz and Bolton, 1972). In general, these radicals are not stable after the temperature is raised above 77 K. The high \( T_A = 873 \text{ K} \) of NO₃ indicates a crystal lattice stabilization of the radical. As with the hydrocarbons, the large NO₃ radical (N-O distance 1.19 Å) can reside in the M site of the feldspar structure.

Generally, the free radicals CH₃, C₂H₅, and NO₃ are not stable above 200 K in fluids; therefore, they cannot be detected in mineral fluid inclusions. In hyalophane and microcline no intracrystalline fluid inclusions in the C-O-H-N system (e.g., CH₄, C₂H₆) were detected by micro-Raman spectroscopic analysis. Because of their high thermal stability (\( T_A = 573-873 \text{ K} \)) and their anisotropic spectra, it is unlikely that the free radicals are located in fluid inclusions or adsorbed at the crystal surface or at intracrystalline cracks. It is generally assumed that \( T_A \) for structurally bonded free radicals in minerals is in the range of 473-773 K. O⁻ and SiO₂⁻ centers in Table 1, which are free radicals by definition, have similar \( T_A \). Furthermore, in all 34 single crystals of hyalophane and microcline studied, the direction cosines of \( g \) and \( T \) tensors of CH₄ and NO₃ centers are the same, and these values are in good agreement with the data of Matyash et al. (1981, 1982).

Moreover, hydrocarbons and NO₃ probably reside at K positions and have \( T_A \) in the same range (573-873 K) in which the detectable Na and K self-diffusion in feldspar begins. It can be concluded that the free radicals studied must be fixed in orientation in the crystal structure.

In polycrystalline samples of feldspar from Volhyn pegmatites, Proshko et al. (1987) observed the typical CH₄ spectrum of very high intensity (Figs. 8, 14c, 14d). Based on the interpretation of Matyash et al. (1981, 1982), the spectra were attributed to NH₄⁺, and this feldspar determined as buddingtonite. Pavlishin and Bagmut (1988) investigated 152 samples of potassium feldspar from different zones of I I pegmatite bodies and surrounding granites. From the intensities of the quartets shown in Figure 8, they concluded an active role for NH₄⁺ in the formation and transformation of minerals of the chambered pegmatites and enclosing granites, and they pointed out that the K⁺/NH₄⁺ ratio of potassium feldspar is an indicator of postmagmatic differentiation of the magmatic material.

Systematic investigations based on many feldspar samples from pegmatite and granite of the Ukrainian Shield showed that in samples that contain methane and ethane, no Fe³⁺ spectra can be detected (Matyash et al., 1981, 1982; Pavlishin, 1983; Proshko et al., 1987; Pavlishin and Bagmut, 1988). Microcline samples from Hagendorf pegmatite also failed to show Fe³⁺ spectra; however, in hydrocarbon-bearing hyalophane, Fe³⁺ centers are present. In the spectra of all hydrocarbon-free feldspars studied so far, Fe³⁺ signals have been observed (cf. Table 1 and references therein). The natural \( P-T \) conditions for the substitution of hydrocarbons in the feldspar structure are unknown. Experimental thermodynamic data for fluids in the C-H-O system are known mainly for high \( P-T \) conditions (e.g., Woermann and Rosenhauer, 1985, and
references therein). Experimental data for mixing in a multicomponent fluid at geologically important P and T conditions are unavailable. Microthermometric and Raman spectroscopic analyses of methane-bearing aqueous fluid inclusions, primarily in pyroxene, garnet, and quartz of skarn facies, indicated trapping T and P of 628–743 K and 1.4–2.5 kbar for garnet, pyroxene, and amphibole skarn (Gerster et al., 1989). Similar homogenization temperatures (663–723 K) were reported by Weisbrod (1982) for methane in pegmatitic quartz.

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