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# Aliphatic hydrocarbons in structural channels of cordierite: A first evidence from polarized single-crystal IR-absorption spectroscopy

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## ABSTRACT

Polarized IR-absorption spectra were measured on inclusion-free spots, 50 μm in diameter of (100)-, (010)-, and (001)-oriented single-crystal plates of orthorhombic cordierites extracted from anatectic granitoids and their pegmatite from the western part of the Ukrainian shield. In the range 3100–2700 $cm^{-1}$, the spectra display four weak ($\alpha_{lin} \leq$ ca. 7 $cm^{-1}$) and sharp ($\Delta\nu_{1/2} \cong 20$ $cm^{-1}$) bands typical of the antisymmetric and symmetric stretching modes of $CH_3^-$ and $–CH_2^-$ groups of aliphatic hydrocarbons, $C_nH_{2n+2}$ ($\nu_{as,CH3}$ at 2951–2959 $cm^{-1}$, $\nu_{as,CH2}$ at 2920–2923 $cm^{-1}$, $\nu_{sym,CH3}$ at 2871–2874 $cm^{-1}$, $\nu_{sym,CH2}$ at 2850–2851). All bands are polarized in the *ac*-plane of orthorhombic cordierite. In the temperature range $123 \leq T$ (K) $\leq 573$, the degree of polarization decreases as temperature increases. The band polarizations and their temperature dependence ensure that the hydrocarbons are incorporated in the cordierite matrix, i.e., in the ca. 5.8 Å wide cavities of the c-parallel channels of the crystal structure. The concentrations of alkanes, $C_nH_{2n+2}$ from band intensities, are between about 20 and about 100 ppm, corresponding to about $0.7 \cdot 10^{-3}$ and about $2.3 \cdot 10^{-3}$ molecules per formula unit cordieriite. Evaluation of the averaged intensities of the antisymmetric as well as symmetric C-H stretching vibrations of either species, $CH_3^-$ and $–CH_2^-$, yields a ratio of 1:1 between them consistent with n = 4 only, realized in butane $C_4H_{10}$ or in a butane-rich mixture with n = 4 on average and concentrations between $0.7 \times 10^{-3}$ to $2.3 \times 10^{-3}$ molecule pfu. Polarizations as well as molecular and cordierite-cavity sizes are consistent with an allocation of butane molecules in the channel cavities of the cordierite structure, with the molecular axes of butane predominantly parallel to **b**.

## INTRODUCTION

Cordierite is a framework alumosilicate with the general formula $(Mg,Fe^{2+})_2^{[6]}[(Al_2Si)Al_2Si_4O_{13}] \cdot n\ X^{chan}$. It is abundant in high-temperature medium-pressure metapelitic rocks, especially of the granulite and high amphibolite facies. The crystal structure (Bystroem 1942; Gibbs 1966) of nearly all cordierites found in nature is orthorhombic with space group *Cccm* and $Z = 4$ formula units per unit cell. It contains six-membered tetrahedral rings, the point symmetry of which is not far from 6/*mmm*. Such rings are stacked over each other along [001]. They are interconnected by additional, $(Al_2Si)$-centered tetrahedra to form a framework that contains, in the "dense structural parts" outside the rings, distorted coordination octahedra, compressed along the internal [111], which allocate the magnesium-, iron- and, if present in subordinate amounts, other cations of appropriate size.

The stacking of the tetrahedral rings along [001] produces channels that run parallel to **c** and have "bottlenecks" of about 2.5 Å diameter at the heights of the mirror plane of the rings, and large cavities between them, with maximum extensions of about 5.4 or about 6.0 Å along [010] or [100], respectively (Armbruster and Bloss 1982). These channels may contain $nX^{chan}$-constituents as sodium and/or potassium-ions (cf. Schreyer 1985), $Fe^{2+}$ as reported by Goldman et al. (1977), or volatiles as molecular water first discovered by Farrell and Newnham (1967) and $CO_2$ (e.g., Armbruster and Bloss 1982). In most cordierites such channel constituents $X^{chan}$ occur in small amounts not exceeding n = 1.

The molecular channel constituents are related to the composition of the coexisting fluid phase (Johannes and Schreyer 1981) during its formation or at closing temperature of diffusion of the respective molecular species. Because this fluid phase may contain hydrocarbons, as obvious from the composition of fluid inclusions in cordierites (Voznyak 1998, personnal communication) and coexisting minerals (e.g., Konnerup-Madsen 1988), the question arises whether such molecules may also be incorporated in cordierite channels. Mass spectrometric analyses of the gases released on heating of cordierites from various *P,T*-regimes, yielded among other species, hydrocarbons (Zimmermann 1981) or $CH_4$ (Kurepin et al. 1986). Infrared absorption spectra obtained on KBr-pressed pellets of powdered cordierites from Dervio-Colico/Como, Italy, displayed C-H vibrations of aliphatic hydrocarbons (Mottana et al. 1983). In all these cases, there exists no proof that the hydrocarbons are indeed occluded in the cordierite channels.

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Here, we report on evidence obtained from polarized infrared absorption spectra on oriented cordierite single-crystal slabs, of the presence of small aliphatic hydrocarbon molecules in the structural channels, on their nature and orientation as well as on the concentration in the cordierite channels.

## MATERIALS AND METHODS

Cordierite single-crystal fragments with 8 mm maximum dimension were extracted from the rocks listed in Table 1. Such cordierites have the characteristics relevant for this work, as also quoted in Table 1 (Kurepin et al. 1986). The crystal fragments were oriented according to their characteristic conoscopic figures such that crystallographically oriented platelets could be produced by grinding and polishing from both sides. The platelets were carefully cleaned in an ultrasonic bath under acetone to remove all traces of organic matter from their surfaces. The platelets were never touched by hand in their further processing. In such a way, cordierite platelets were obtained allowing for polarized measurements, as shown in Table 2.

Polarized IR-absorption spectra were scanned in the spectral range 3100–2700 $cm^{-1}$, wherein C-H stretching modes of hydrocarbons produce absorption bands of high molar absorptivities (Nakanishi and Solomon 1977), by means of a Fourier-transform interferometric spectrometer (Bruker IFS 66) with a KBr beam-splitter and attached IR-microscope (Bruker IRScope I) allowing for measurements of areas with diameters down to about 50 μm. The microscope was equipped with 15× Cassegranian mirror optics, a polarizing foil, and an $LN_2$-cooled MCT detector. The instrument, especially the microscope, was permanently flushed with air cleaned from $H_2O$ and $CO_2$ to reduce intensity loss of the beam and avoid interference from effects of slight incompensations between reference $I_0$ and subsequent sample I measurements. Spectral resolution was 2 $cm^{-1}$. A heating-cooling table (Lincam FTIR 600) allowing for measurements in a range of about 100–600 K, was placed in the object plane of the microscope. The cordierite platelets were held in the object plane on copper-wire grids. The $I_0$-reference measurements were obtained without sample in air and 120 scans were averaged. As the C-H bands are very weak with absorptivities ($\alpha = \log(I_0/I)/t$, with t = plate thickness in centimeters) not exceeding 8 $cm^1$, spectra from several spots on the same plate were repeatedly measured, reproducibility was confirmed. Utmost care was used to avoid fluid inclusions or cracks. Appropriate cross checks excluded traces of organic contaminants on the plates' surfaces and/or in fluid inclusions.

## RESULTS AND DISCUSSION

### Single-crystal spectra of the cordierites in the C-H stretching range and their assignment

Four weak and sharp bands are observed in polarized spectra of the cordierites (Fig. 1). These are the well-known antisymmetric or symmetric C-H stretching vibrations in $CH_3^-$ and -$CH_2^-$ groups of aliphatic hydrocarbons (e.g., Nakanishi and Solomon 1977): (I) $\nu_{as}$ of $CH_3^-$ occurs at 2951–2959 $cm^{-1}$; (II) $\nu_{as}$ of –$CH_2^-$ is at 2920–2923 $cm^{-1}$; (III) $\nu_{sym}$ of $CH_3^-$ is at 2871–2874 $cm^{-1}$; and (IV) $\nu_{sym}$ of –$CH_2^-$ is 2850–2851 $cm^{-1}$. All have band widths of about 20 $cm^{-1}$. These assignments are also shown in Figure 1. The spectra do not show a band at 3019 $cm^{-1}$, where the IR-active antisymmetric C-H stretching vibration of $CH_4$ would be expected (Nakamoto 1986) when methane molecules were present in the channels. Also, C-H vibrations near 3050 $cm^{-1}$ typical of aromatic hydrocarbons, in our case benzene $C_6H_6$ (e.g., Nakanishi and Solomon 1977), are absent in the spectra.

The bands in the spectra are clearly polarized in the *ac*-plane of the cordierite crystals, though the polarization is incomplete (Fig. 1; Table 3). The degree of polarization increases with decreasing temperature as seen by visually comparing the intensities of bands in **E**||**b** and **E**||**c** with each other and for both temperatures, 293 and 173 K, (Fig. 1, bottom). This deduction is confirmed by comparing the ratios of integral intensities over background between 2993 and 2813 $cm^{-1}$, $\alpha_{int}(\mathbf{E}\|\mathbf{c})/\alpha_{int}(\mathbf{E}\|\mathbf{b})$: this ratio increases from 1.0 at 293 K to 2.4 at 173 K. These observations prove that the hydrocarbons are occluded in the cordierite matrix, i.e., in the structural channels. They are neither related to remnants of traces of organic matter from polishing, nor are they caused by hydrocarbons in fluid inclusions because for these two cases, the bands would not be polarized. As an additional test, we measured randomly oriented, freshly extracted crystal fragments that did not have any contact with organic matter. The spectra of such fragments showed bands similar to Figure 1 with low intensities, though, of course, unpolarized. Hence, surface contaminations of the cordierite platelets do not cause the bands in Figure 1. Furthermore, we deliberately set the measuring beam on a spot wherein fluid inclusions could be seen in the microscope. As a result, the intensity of the C-H bands were higher by factors around 2, and the polarizations of the bands were nearly lost. All these observations clearly prove that the C-H stretching bands (Fig. 1) originate from aliphatic hydrocarbons within the cordierite structure channels.

**TABLE 1.** Host rocks and chemical characteristics of the corderites studied

| Rock type | Temperature of formation (˚C)* | Sample no. | Cordierite characteristics† | | |
|---|---|---|---|---|---|
| | | | Fe / (Mg + Fe) | $H_2O^{chan.}$ (pfu) | $CO_2^{chan.}$ (pfu) |
| anatectic granite | 780 | 1201 | 0.22 | 0.084 | 0.103 |
| anatectic granite | 780 | 56-81 | 0.20 | 0.135 | 0.035 |
| granite-pegmatoid | 730 | 39-83 | 0.27 | 0.091 | 0.117 |
| pegmatite | 600 | 9-81 | 0.46 | 0.231 | 0.051 |

* Kurepin et al. (1986).

† Molecular water and $CO_2$ contents held in the structural channels of the cordierite studied, as determined by mass spectoscopy after preheaing at 500-600˚C, were taken from Kurepin 1991. Their data, given in weight percent, were recalculated to $mol_{H_2O}$ or $mol_{CO_2}$, respectively, per $mol_{cordierite}$ (the same as per formula unit).

**TABLE 2.** Orientations and thicknesses of cordierites prepared for IR-measurements with the quoted orientations of the readiations electrical vector

| Rock no. | Cordierite plates Thickness in µm | Measurements possible |
|---|---|---|
| 1201 | (010)/210 | E\|\|a and E\|\|c |
| | (001)/80 | E\|\|a and E\|\|b |
| 56-81 | (010)/100 | E\|\|a and E\|\|C |
| | (100)/90 | E\|\|b and E\|\|c |
| 9-81 | (001)/450 | E\|\|a and E\|\|b |
| 39-83 | (100)/265 | E\|\|B and E\|\|C |

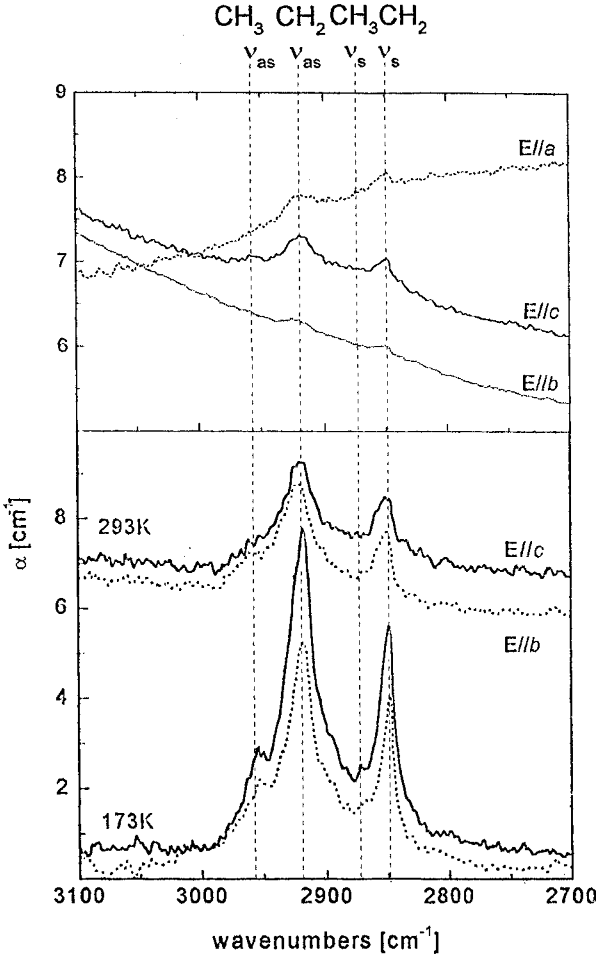

**FIGURE 1.** Single crystal IR-absorption spectra scanned in the spectral range of the C-H stretching vibrations of hydrocarbons on crystallographically oriented platelets of cordierites from the Ukrainian shield (cf. Table 1). The spectra were scanned at ambient conditions with the measuring beam polarized **E**||**a**, **b**, or **c** in cordierite plates from (010), (001), and (010) faces, respectively, of rock 1201 (upper part) or at ambient and low temperature in polarizations **E**||**b** and **c** in a cordierite (100) plate from rock 56-81 (lower part). The measuring spot was 50 mm in diameter and was set on parts of the crystal plates that were free of fluid inclusions, cracks, etc. Note that the ordinates give absorbances normalized to 1 cm (linear absorption coefficient, $\alpha = \log(I_o/I)/t$ with t = plate thickness in centimeters). Band assignments are given above the figure.

## Nature of the aliphatic hydrocarbons and their allocation in the cordierite channels

We neither observed the IR-active antisymmetric stretching vibration of $CH_4$ nor C-H stretching vibrations of aromatic hydrocarbons, benzene. However, we did observe the C-H vibrations $\nu_{as}$ and $\nu_{sym}$ of both $CH_3^-$ and $-CH_2^-$. Hence, alkanes $C_nH_{2n+2}$ with $n > 2$ must be the molecules in the channels.

The predominant polarization of these bands in the *ac*-plane of the cordierite matrix (Table 3) indicates that the molecular axis of the lowest-energy linear equilibrium form of the occluded alkane molecules is predominantly oriented parallel to [010]. This follows from a symmetry analysis (discussed below) of the vibrations of the molecules.

The size of the large cavities in the channels in combination with the molecular sizes of linear alkane molecules sets n to maximum of 4 for molecules with observed polarization of the C-H vibrations, i.e., to butane which has a linear equilibrium form that is 5.40 Å long between the centers of the two terminating hydrogen atoms (Schmalz 1998, personal communication). The incomplete polarization may indicate minor amounts of larger molecules the axes of which will, for size reasons, be parallel to [001] and create an *ab*-polarization of their C-H stretching vibrations. In high temperature spectra up to about 550 K not to be reported in detail here, band intensities in **E**||**b** polarization are even growing over those in **E**||**c** with raising temperature, an effect that is reversible. At about 650 K, the bands disappear irreversibly. These observations could point to an increasing reorientation of the molecular axes along [001], which is reversible on temperature decrease when the temperature did not exceed ca. 550 K, and a release of the hydrocarbon molecules from the channels at temperatures above ca. 600 K. These observations resemble the behavior of $H_2O$ and $CO_2$ in cordierite channels on heating (Aines and Rossman 1984).

That butane is the predominant alkane species is obvious also from an additional argument, derived from a quantitative evaluation of band intensities: we measured the linear absorption coefficients, $\alpha = \log(I_o/I)/t$ (t = plate thickness in centimeters), over background in the maxima of the two C-H bands of $CH_3^-$ as well as of $-CH_2^-$ in the spectra polarized along **a**, **b**, or **c** and we calculated mean linear absorption coefficients for the isotropic case as $\bar{\alpha} = (\alpha_{||a} + \alpha_{||b} + \alpha_{||c})/3$ for the four bands. These $\bar{\alpha}$-values are quoted in Table 3 and allow for the calculation of the concentrations of the $CH_3^-$ and $-CH_2^-$ of the molecular species in the cordierite matrix using the molar absorptivities of the C-H stretching vibrations of such groups as given by Nakanishi and Solomon (1977). The concentrations can be expressed in weight parts per million and, if so, sum up to values of about 20 ppm alkane in cordierite from rock 1201 and about 100 ppm in cordierite from rock 56-81. However, it is more informative to calculate the concentration of either species $CH_3^-$ and $-CH_2^-$ in the occluded molecules as moles per formula unit of cordierite. This was done for both the antisymmetric and symmetric vibrations. The c-values obtained are quoted in Table 3 and were averaged. (In principle, the concentrations obtained for $CH_3^-$ and $-CH_2^-$ from both their C-H vibrations, the asymmetric and the symmetric should be the same. Table 3 shows that they are indeed close to each other except that $\nu_{as}$, yields too low a concentration of $CH_3^-$ in cordierites from rocks 1201 and 39-

**TABLE 3.** Polarization and intensities of symmetric and asymmetric C-H stretching vibrations of $CH_{\bar{3}}$ and $–CH_{\bar{2}}$ as well as their concentrations in the structural channels of the cordierites studies

| Sample no. | | $CH_{\bar{3}}$ | | | $–CH_{\bar{2}}$ | | |
|---|---|---|---|---|---|---|---|
| | | $\nu_{as}$ | | $\nu_{sym}$ | $\nu_{as}$ | | $\nu_{sym}$ |
| 1201 | polarization | $c > a > b$ | | $c > a > b$ | $a \cong b \cong c$ | | $c > a > b$ |
| | $\bar{\alpha}(cm^{-1})$* | 0.1 | | 0.13 | 0.3 | | 0.23 |
| | $\underline{C}$ (pfu)·$10^3$† | 0.3 | | 1.0 | 0.9 | | 1.2 |
| | $\bar{C}_{as,sym}$(pfu)·$10^3$ | | 0.7 | | | 1.1 | |
| 56–81 | polarization | $a > c > b$ | | $c \cong a >> b$ | $a > c > b$ | | $c \cong a > b$ |
| | $\bar{\alpha}(cm^{-1})$ | 0.32 | | 0.27 | 0.7 | | 0.47 |
| | $\underline{C}$ (pfu)·$10^3$ | 1.1 | | 2.1 | 2.2 | | 2.4 |
| | $\bar{C}_{as,sym}$(pfu)·$10^3$ | | 1.6 | | | 2.3 | |
| 9-81 | polarization | n.m.‡ | | $a > b$ ($c$, n.m.) | $a > b$ ($c$, n.m.) | | $a \cong b$ ($c$, n.m.) |
| | $\bar{\alpha}(cm^{-1})$ | | | 0.12 | 0.4 | | 0.3 |
| | $\underline{C}$ (pfu)·$10^3$ | | | 0.9 | 1.2 | | 1.6 |
| | $\bar{C}_{as,sym}$(pfu)·$10^3$ | | 0.9 | | | 1.4 | |
| 39-83 | polarization | $c > b$ ($a$, n.m.) | | $c > b$ ($a$, n.m.) | $b > c$ ($a$, n.m.) | | $c \geq b$ ($a$, n.m.) |
| | $\bar{\alpha}(cm^{-1})$ | 0.07 | | 0.2 | 0.3 | | 0.15 |
| | C (pfu)·$10^3$ | 0.2 | | 1.6 | 0.9 | | 0.8 |
| | $C–_{as,sym}$(pfu)·$10^3$ | | 0.9 | | | 0.8 | |

* Intensities are given as mean values of linear absorption coefficients $\alpha$ [$cm^{-1}$=log($I/I_0$)t, where t = plate thickness in cm, at ban maximum over backgound. The mean values are obtained by averaging the a-values of bands in the polarized spectra with E||*a*, *b*, and *c*.

† Concentrations $C_{CH3}$ and $C_{CH2}$ are given in mole per formula unit of cordierite. These were recalculated from the original [mole/1000 $cm^3$ cord] which were obtained from the mean absorption coefficients using the relation $C_{H2,CH3}=\alpha_{CH3},_{CH2}/\varepsilon_{CH3},_{CH2}$, where $\varepsilon$ were the molar absorptives in [l·$mol^{-1}$·$cm^{-1}$] as given in Nakanishi and Salmon (1977).

‡ n.m. = not measured because of ditection limits and/or lack of appropriate crystal slab.

83. The reason is that the respective bands have very low intensity with $\alpha \leq 0.1$ $cm^{-1}$, which results in large errors.) Those concentrations are close to the ratio 1:1 (Table 3) in the cordierite crystals from the four rocks of Table 1. This result confirms the presence of butane again when there is only one type of alkane molecules present in cordierite. However, it is also possible that alkanes with n = 2 and n = 3 mixed with alkanes with n > 4 in molar fractions, which would produce an overall ratio of $CH_{\bar{3}}$:$–CH_{\bar{2}}$ = 1:1, might also account for the result.

On the other hand, the combination of the three arguments the size argument, the polarization argument, and the above analyses, comprise strong support that butane oriented parallel to [010] is the predominant aliphatic hydrocarbon occurring as trace amounts in the cordierite channels. The geometry of the butane molecule (Schmalz 1998, personal communication) shown in Figure 2 is that of the lowest-energy configuration. The C-C and C-H distances and angles and the dimensions of the whole molecule are in-scale with the dimensions along *b* of the cages and of the "bottlenecks" of the cordierite channels (Armbruster and Bloss 1982). This scale is also shown in Figure 2. However, the hydrogen atoms are not shown with their real radius for the sake of clarity. If the van der Waals radius for the 2 H atoms are added then the largest extension of the molecule in its lowest energy configuration is 7.8 Å. Thus, the molecule tightly fits into the widest opening of the cavity (cf. Fig. 2). These sizes are only approximate ones as they depend on the choice of the type of the radii of O atoms forming the outer channel "walls" as well as of the terminating hydrogens of the alkane molecules.

The orientation of butane in Figure 2 was derived from a symmetry analysis of the lowest-energy form of this molecule and the C-H vibrations of its $–CH_{\bar{2}}$ and $CH_{\bar{3}}$ groups: the molecule has the point symmetry $C_5$ with the mirror plane m cutting through the C-atoms of the zigzag chain formed by the four carbon atoms. Further, m is oriented within the molecule

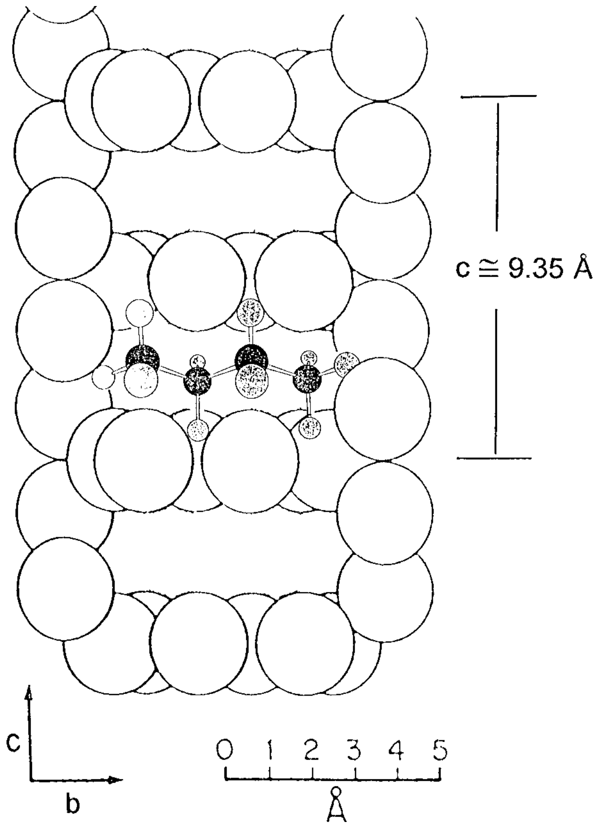

**FIGURE 2.** Allocation and orientation of butane, as evaluated from band polarizations and band intensities, in a cavity of channels parallel to **c** in orthorhombic cordierite. The geometry of the channel is from Armbruster and Bloss (1982). The geometry of the lowest-energy equilibrium form of butane is shown, the dimensions are in size with the scale displayed in the lower right (cf. text).

such that the two hydrogen atoms of each of the two $–CH_2^-$ groups are symmetry equivalent by m as well as two out of the three hydrogen atoms of the two terminating $CH_3^-$ groups. The last of the three hydrogen atoms of each of these $CH_3^-$ groups lies within m. This geometry leads to the following orientations of the dipole moment vector, $\delta\mu$, of the vibrational transitions in the $–CH_2^-$ and $CH_3^-$ groups, the character of which is also given:

| | | | |
|---|---|---|---|
| $–CH_2^-$ | $\nu_{as}$ | $(B_1)$ | $\delta\mu \perp$ molecular axis and in plane of m |
| | $\nu_{sym}$ | $(A_1)$ | $\delta\mu \perp$ molecular axis and out of plane of m |
| $–CH_3^-$ | $\nu_{as}$ | (E) | $\delta\mu \perp$ molecular axis and in plane of as well as out of plan of m (degenerate) |
| | $\nu_{sym}$ | (A') | $\delta\mu \parallel$ molecular axis and in plane of m |

The combination of these results with the relevant properties of the cordierite structure yields polarizations of $\nu_{as}$ and $\nu_{sym}$ expected for the various possible orientations of the butane molecules inside the channel cavities (Table 4). The observed C-H band polarizations (Table 3) are best met by the theoretical predictions when the butane molecular axis parallels **b** or [010] and m parallels (100) or (001). An orientation of the molecular axis along the channels, i.e., ||**c** or [001], can be excluded as the intensities would be expected to be lowest for **E**||**c**-measurements whereas they are the in fact the highest (cf. Table 2). Table 4 shows further that the molecular orientation parallel **a** or [100] is also unlikely. As a result, the butane orientation inside the cavities of the cordierite channels may be shown as in Figure 2.

It is perplexing as to why the molecular axes would be oriented along **b** when there is more space in the channel cavities along **a** (cf. Gibbs 1966). We tentatively propose that the hydrocarbon molecules, which are known to form weak hydrogen bridges with appropriate acceptor atoms, may be more strongly attracted by the underbound O atoms connecting Al- and Si-centered ring tetrahedra of the Al-Si ordered cordierite structure (Gibbs 1966) than by the O atoms connecting two Si-centered ring tetrahedra. Oxygen atoms of the former type are found along **b**, not along **a** in Al-Si ordered orthorhombic cordierites.

**TABLE 4.** Polarizations of the C-H stretching vibrational bands of $–CH_2^-$ and $Ch_3^-$ groups of butane molecules in their lowest-energy configuration, when included with the indicated orientations in cavities of the *c* parallel structural channels of chrdierite (cf. text)

| Orientation of the butane molecule* | | $–CH_2^-$ | | $CH_3^-$ | |
|---|---|---|---|---|---|
| Molecular axis | m | $\nu_{as}$ (B1) | $\nu_{sym}$(A1) | $\nu_{as}$ (E) | $\nu_{sym}$ (A') |
| \|\| [100] | \|\| (010) | b | c | (c,b) > a | a |
| \|\| [100] | \|\| (001) | c | b | (c,b) > a | a |
| \|\| [010] | \|\| (100)† | a | c | (c,a) > b | b |
| \|\| [010] | \|\| (001)† | c | a | (c,a) > b | b |
| \|\| [001] | \|\| (100) | a | b | (a,b) > c | c |
| \|\| [001] | \|\| (010) | b | a | (a,b) > c | c |

* With respect to corierite crystallographic axes.
† These orientations best fit the observed polarizations (Table 2).

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